

ISSN 0024-4902

Vol. 22, No. 3, May-June, 1987

January, 1988

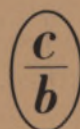
LTMRAR 22(3) 209-310 (1987)

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

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Subscription (6 Issues)

Vol. 21: \$645 (domestic); \$715 (foreign)
Vol. 22: \$715 (domestic); \$790 (foreign)

Single Issue: \$150
Single Article: \$12.50

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER: Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

CONSULTANTS BUREAU, NEW YORK AND LONDON



233 Spring Street
New York, New York 10013

Published bimonthly, consisting of Volume 21 issues 3 through 6 and Volume 22 issues 1 and 2. Subscription price for Volume 21 is \$645, and for Volume 22 \$715. Second class postage paid at Jamaica, New York 11431.

LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

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May-June, 1987

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The Russian press date (podpisano k pechaty) of this issue was 5/15/1987. Publication therefore did not occur prior to this date, but must be assumed to have taken place reasonably soon thereafter.

Lithological and mineralogical data are presented in this article characterizing the features of sediment formation in the Tadjhur rift which are connected with spreading and the appearance of oceanic crust. The main background sediments at depths greater than 2000 m are represented by lime-clay and clay-lime deposits. Terrigenous material is primarily of eolian genesis. Anomalies in the circulation of the gulf's water masses affect the wide distribution of reduced muds.

The Gulf of Aden is a relatively narrow, moderately deep body of water. The Sheba ridge occurs in its axial portion, tracing the active rift (spreading) zone (Fig. 1); oceanic crust is formed here which is traceable under a large portion of the gulf. On the east, the Sheba ridge connects in a complicated manner with the Carlsberg ridge, which belongs to the mid-ocean ridge of the Indian ocean.

Moreover, the Aden rift zone divides the Somalian and Arabian continental plates rather than oceanic plates, and it is sometimes considered as an incipient ocean. On the west it enters a rift triple junction system, receiving the name the Afar triangle; here the Aden and Red Sea rifts (marine) join with the intracontinental Ethiopian rift [1, 3, 11].

The structure of the western portion of the Gulf of Aden is somewhat distinct from the rest of its territory. The axial ridge is not traceable here, but the rift is sharply expressed, and it has received the name Tadjhur. It is unique in its relations, in that it immediately develops into the intercontinental Azal' rift. In hypsometric plan, the Tadjhur rift is characterized by overall elevation, with relatively lower framing uplifts and low intensity of basaltic extrusion.

Many articles have been devoted to the geology of the Aden rift system, but they are mainly concerned with tectonics and magmatism. Questions of sedimentation have been only lightly touched upon, and they are principally related to the region which lies to the east of the Tadjhur region [6].

Here in 1983-1984, complex geological-geophysical and lithological investigations were conducted by the Institute of Oceanology of the USSR Academy of Sciences under guidance of A. P. Lisitsyn [the 7th voyage of the NIS (Scientific-Research Station) Akademik Mstislav, Keldysh]. A polygon defined by the coordinates 11°52'-12°11' N lat. and 44°35'-45°11' E long. was spanned by detailed efforts. The size of the polygon is 35 × 67 km.

Study of the sediments was based on material selected by bottom tubes (60 stations) and floor dredges (25 stations); the maximum tube length was 6 m. In addition, observations accomplished during trips of manned underwater apparatuses "Pisces" were considered [4].

Stratigraphic separation of sections was carried out with the aid of foraminiferal analysis (data of Kh. M. Saidova) and radiocarbon determinations of absolute sediment ages were widely utilized (data of V. M. Kuptsov).

BASIC RIFT ZONE STRUCTURE

In the studied region, the rift zone has a sublatitudinal trend, and it is comprised of an inner rift or rift valley, with a staircase of fault terraces bounding it to the north and south (Fig. 2) [1, 3].

The inner rift is from 4 to 9 km wide and 1200 to 1480 m deep. A narrow (1-2 km) band of extrusions occurs in its axial portion, distinguished from the faulted terraces by edge

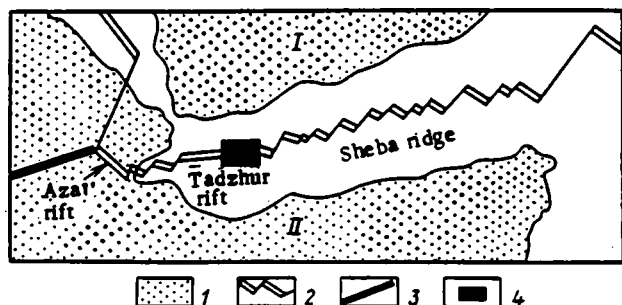


Fig. 1. Scheme illustrating the position of the Tadjhur rift. 1) Plates: I) Arabian plate; II) Somalian plate; 2) rifts; 3) transform faults; 4) study area.

depressions. This is approximately bounded by the 1150 m isobath, and is 4-5 km wide; from seismic data, the sediment thickness reaches 50 m in places.

The extrusive band is formed by a network of volcanic uplifts, the peaks of which are located at depths from 1250 to 1000 m, elevated above the adjoining depressions by 50-100 or 200-250 m; structures range from 0.5×1 to 1×3.7 km in size. All extrusions are formed of tholeiitic basalts. Tectonic faulted terraces 180-200 m in height also occur in the inner rift.

The bounding terraces lie at depths from 500-700 to 1000-1100 m. They have steep slopes, facing toward valleys, and gently sloping back slopes (terraces), partially leveled by sediments. The width of the main terraces ranges from 1-2 to 5 km, and the height is generally 100-200 m, seldom up to 400 m. They may vary in hypsometric level and interlink with one another. The main terraces are often complicated by more finely faulted terraces. Basalts are exposed in the upper portions of the steep slopes, while lumpy talus from basaltic clastics develops lower.

Two zones of transverse faulting trending southwest are established in the studied polygon. One of these lies on the west, other on the east portion of polygon.

CHARACTERISTICS OF DEPOSITS

Sediment Types. Clay and calcareous materials are the main sediment forming components. The CaCO_3 content generally varies within the limits of 40-60%, seldom falling below 21% or exceeding 70%. Before lithification the largest portion of the sediments may be classified as marls. Carbonate material is represented by coccoliths (predominantly) and foraminifera. A thin organogenic slurry and coarser, different appearing detritus (pteropods, mollusks, and corals) have a lesser value. The terrigenous fragmental component (siltstone, fine sandstone) is as a rule sparsely represented by scattered grains, but over a fixed interval their quantity noticeably increases. Radiolaria and diatoms are seldom encountered, while siliceous sponges occur often. Terrestrial plant detritus is noted in a small quantity. Basaltic hyaloclastics and volcanoedaphogenic material are locally present.

After granulometric analysis, the mineral composition of the coarse silt sediment fractions were studied in detail in the heavy and light subfractions. It was established that sediments here are unusually identical, as a result of similar conditions of sediment accumulation (depth, CaCO_3 productivity, and small variations in the supply of material from dry land).

The fact that the Gulf of Aden is in an arid zone determines the eolian nature of the terrigenous minerals in its sediments. It is established that a significant portion even of the carbonate material in the gulf deposits (and in the Arabian sea) was a continental (eolian) genesis [5, 12].

The terrigenous contribution to the sediments is provided by wind from both sides of the Gulf of Aden (from the Arabian peninsula and the north part of the African continent), and is due to by the respective petrographic composition of the rocks developed in these regions.

Two main mineral complexes are distinguished: 1) granito-gneissic (quartz, feldspars, micas, zircon, apatite, tourmaline, garnet, staurolite, kyanite, rutile, sphene, and other minerals), and 2) greenschist (minerals of the epidote group and amphiboles, including tremolite-actinolite and monoclinic pyroxene).

The larger portion of quartz and feldspars from the Gulf of Aden is associated with the sedimentary rock complex; the rocks of the basic and ultrabasic series have a subordinate value in terms of the supply of sedimentary material. The primary minerals of the carbonateless

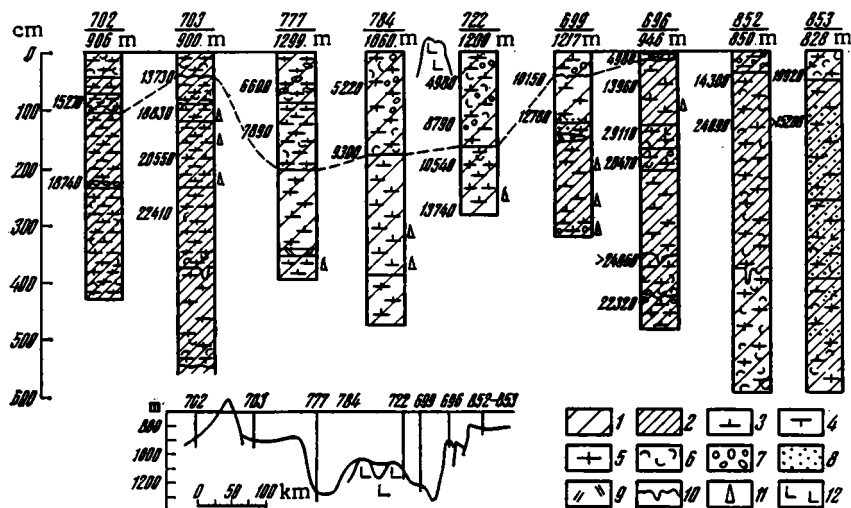


Fig. 2. Sections along a transverse profile, across the rift zone. 1-5) muds [1) clay-carbonate; 2) carbonate-clay; 3) coccolithic; 4) foraminiferal; 5) foraminiferal-coccolithic]; 6) admixture of various shelly detritus; 7) pelletal sediments; 8) admixture of terrigenous silt; 9) basaltic clastics; 10) rough contacts; 11) abundant sponges; 12) basalts. The station number is shown in the numerator and the depth in meters is shown in the denominator above the core samples; the numbers on the left are the absolute age.

portions of sediments from the Tadzbur rift are quartz, feldspars, and micas (principally biotite).

The heavy subfraction, generally comprising a fraction of a percent, seldom 5-6%, and in isolated cases more than 10%, is predominantly composed of monoclinic pyroxenes, ordinary hornblende, minerals of the epidote group, and dark ore minerals.

Within the limits of the southern tectonic terrace (station 702), the quartz content over every length of core sample is quite constant and varies within very small limits — from 37.3 to 46.9%; on the northern tectonic terrace (station 853), the quartz content is somewhat lower, while its variations are also insignificant (27.5-38.0%).

In the central portion of the depression, in the extrusive zone and close to it (stations 734, 756, 763, 777, 790, and 795), the quartz quantity varies widely, reaching 52.8% (station 734, horizon 10-20 cm), but it nowhere decreases below 20%. Quartz grains in the sediments are primarily fresh and angular, but they are also often rounded, of a milky-white color variety, sometimes with dark inclusions (ore minerals, rutile and others); grains covered by a film of iron hydroxide also occur. Both plagioclases and potassium feldspars, most of all microcline, are distinguished amid the feldspars.

On the whole, x-ray diffractometric study of samples showed that in the majority the ratio of plagioclases to potassium feldspars is equal to 2.3:1. The total quantity of feldspars in the composition of the light subfraction on an average reaches nearly 20%, and variations in the contents are insignificant.

Micas are an important group of minerals in sediments of the Tadzbur rift. They are most often represented by green and brownish-green biotite; muscovite and chlorite are noted almost constantly, but in significantly smaller quantities. Sheets of biotite are always well rounded, and in several cases they have dark point inclusions. The refractive index in a majority of cases is equal to approximately 1.63, which indicates that this mineral belongs to the iron rich variety. Einsels and Werner [8] recorded biotite in Ethiopian sands, from which this mineral is transported by wind into sediments in the Gulf of Aden.

Glauconite is detected in small quantities in the sediments. Its nature is apparently secondary. This is both an authigenic mineral, filling shells of foraminifera, and rounded — allochthonous, brought by wind from the Aden peninsula along with biotite.

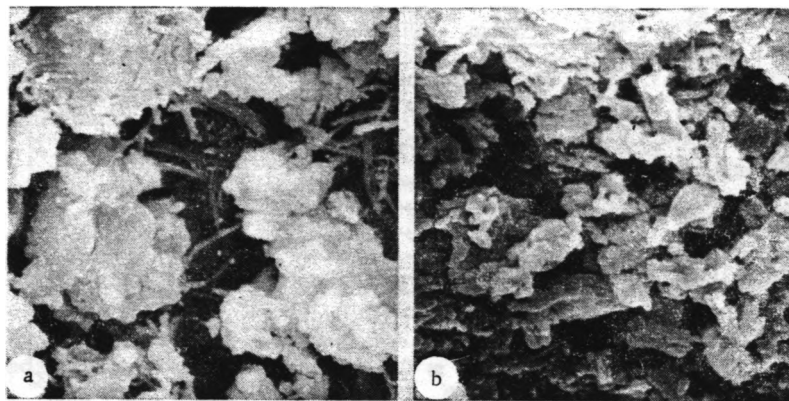


Fig. 3. Electron-microscopic photos of eolian material, sampled above the Gulf of Aden: a) palygorskite; b) quartz, feldspars, $\times 4000$.

Rhyolite-andesitic glass is an almost constant component of the sediments (refractive index $n' = 1.500-1.502$). Its sources are Quaternary rocks of the Aden volcanic series.

Ordinary (green) hornblende, pyroxenes (primarily augite), minerals of the epidote group, dark ores, and apatite predominate amid the heavy minerals of continental genesis, comprising no more than 6% of the coarse silt fraction. Accessory minerals and generally represented by zircon, sphene, and tourmaline, while minerals of the metamorphic complex (kyanite, staurolite, andalusite) were almost constantly noted. The total quantity of these minerals seldom exceeds 1%. Terrigenous carbonate material plays a significant role in the composition of the coarse silt sediment fraction of the Gulf of Aden. Amid this is recorded dolomite with the form of semirounded rhombohedral and irregular grain forms.

On the whole, the composition of the coarse silt portion of the terrigenous sediments from the Tadjur rift reveals a similarity to the composition of coarse silt eolian material collected above the Gulf of Aden and the Arabian Sea.

The heavy minerals contribute olivine, a portion of the pyroxenes, and ore minerals to the edaphogenic components, while the light minerals contribute plagioclases, zeolites, basic glass, and palagonite.

The composition of clay minerals in fractions finer than $1\ \mu\text{m}$ was studied in eight test cores traversing different zones of a fault, as well as on its flanks. After removing carbonates from the sample, the x-ray diffractometric data showed the presence of Al-Fe montmorillonite with predominance of the ferrous variety (25-40%), illite (16-34%), palygorskite (15-37%), and chlorite (6-20%), and a significant quantity of quartz and feldspars. Morphological features of eolian material are shown in electron-microscopic photos (Fig. 3a, b). There is no systematic vertical variation in the relationship of the group of clay minerals to the test cores. Along the flanks of the fault the illite content is somewhat greater than in the depression, while montmorillonite presents the reverse picture. These data were compared with x-ray recordings of the noncarbonate fractions $<1\ \mu\text{m}$ of an eolian suspension which was selected above studied region. Mineral reflections from the eolian suspension have larger intensity and lesser background. This indicates a lesser dilution by amorphous material takes place in the sediments, apparently, owing to the volcanogenic glasses. The main clay mineral components of the eolian material are: illite 40% and palygorskite 34%; chlorite and montmorillonite are found as slight impurities. Quartz and feldspars are found among the nonclay minerals. This direct comparison is uniquely indicative of an eolian source of highly dispersed minerals. Montmorillonite presents some exceptions, since it is noticeably less in the eolian material than in the sediment. It is necessary, however, to take into account the fact that the atmospheric material reflects the exact moment of its sampling, while the sediment gives a many-year reflection. It is possible to suppose that a small portion of the montmorillonite originated from in place on the basalts of the fault zone. Electron-microscopic photographs of basalts demonstrate their essential change into the fibrous-mesh formations characteristic of authigenic smectite. A low spreading rate and significant rate of sediment formation veil specific features of hydrothermal phenomena in the composition of clay minerals.

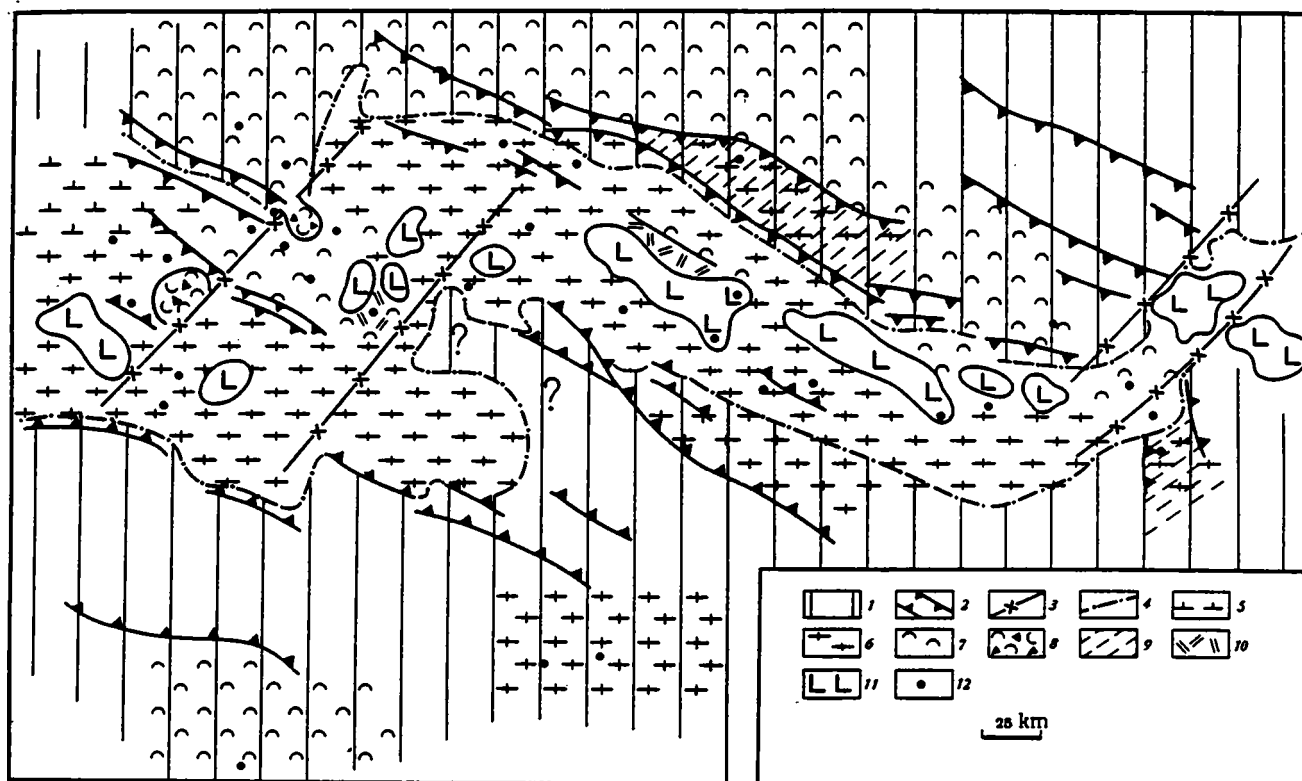


Fig. 4. Map of the position within the polygon of sediments from the first sequence (Holocene). 1) terraces; 2) faults; 3) transverse faults; 4) boundary of rift valley; 5) pelitic clay-coccolith muds (first type); 6) clay-coccolith muds with foraminifera (second type); 7) clay-coccolith muds with various shelly detritus (third type); 8) deposits with rhythmic stratification; 9) accumulations of basaltic clastics; 10) basaltic field; 11) base stations; 12) base stations.

As was shown earlier [2], clay mineral compositions in the Gulf of Aden and the Red Sea differ sharply. In generalizing articles on clay mineral composition in surface sediment layers of the Arabian Sea [9, 10], it was shown that material from the deserts of Southern Arabia and Somalia, and partially from the coast of the Makhran, enters into the western region. These sources supply primarily quartz, illite, palygorskite and chlorite. An appreciable quantity of montmorillonite is carried out from the Dekkan plateau in the winter when northeast winds blow across India, and in the summer by southwest winds from Africa and the Arabian peninsula.

The following major sediments types are distinguished dependent on the relationships of various components.

1. Pelite, carbonate-clay, and clay carbonate muds; the carbonate composition is formed primarily by coccoliths, but an admixture of fine shelly slurry and pelagic foraminifera is often contained. The CaCO_3 content increases with increase of the admixture (up to 60%), and pelitic structure changes into silty-pelitic. The sediments are green-grey, from light to dark, marsh-green. Bioturbation is characteristic, causing a random texture, mottling, and nodular appearing accumulations of shell material; pelletal areas are often observed. Here and there are many sponges, both separate spicules and columnar. Pteropods and thin valved mollusks are encountered. There are many dark point precipitations of iron sulfides (framboids) on specific intervals. There is generally very little terrigenous silt, but on several levels its quantity increases noticeably, often reaching 20-25%.

2. Clay-carbonate muds, outwardly resembling those examined above, but with a lower pelite content (15-50%), corresponding to granulometric pelite-silt and sand-silt varieties. The basic sediment forming components are shells of foraminifera, in some cases fine, in others coarse (0.05-0.5 mm); planktonic forms predominate sharply, but benthic forms also exist. Pteropods are constantly present, (complete shells and fragments), while other skeletal re-

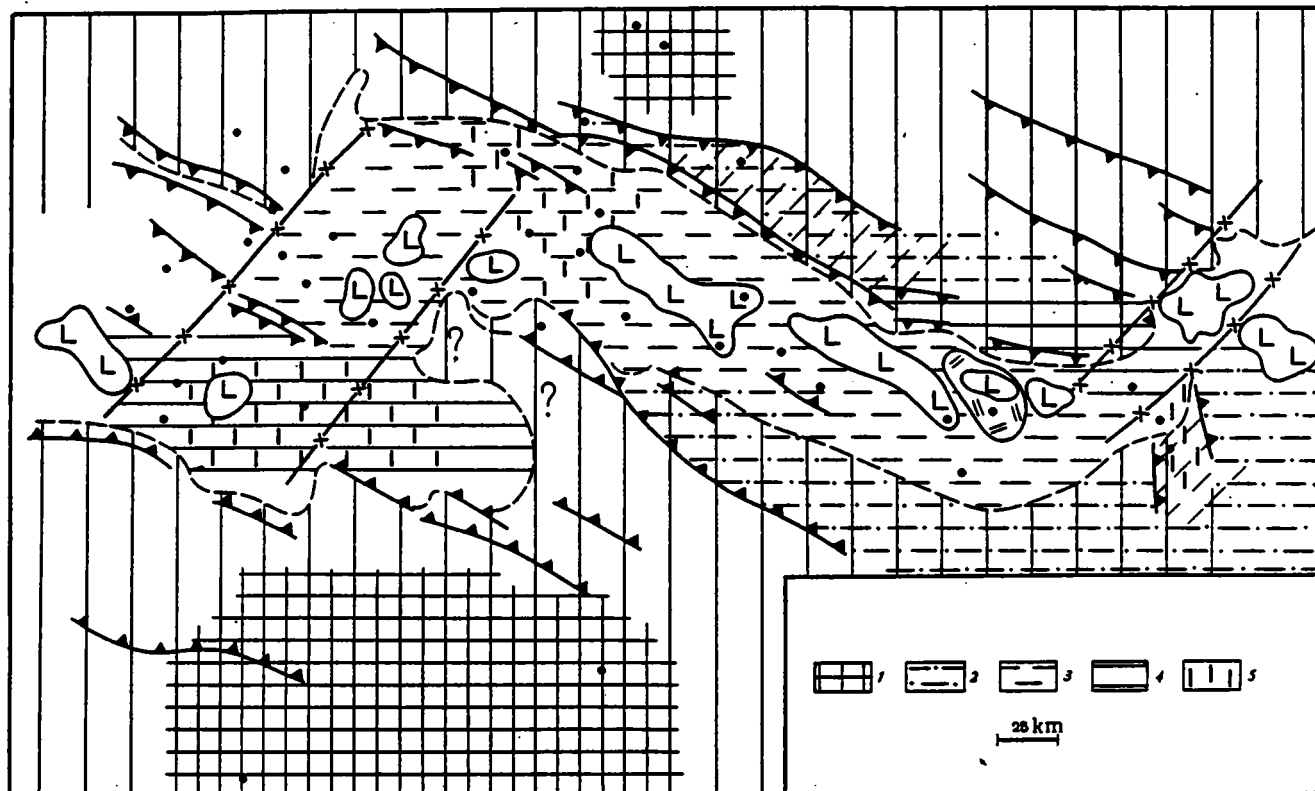


Fig. 5. Map of the position of sediments from the second sequence (10,000-12,000 years). 1) Absent sediments (eroded); 2-4) clay-coccolith muds; 2) little thickness, particles diffused; 3) thickness 50-100 cm; 4) thickness greater than 100 cm; 5) field of sponge development. The remainder of the legend is as in Fig. 4.

mainders (mollusks, spicular skins) are also present in small quantities; here and there are many pellets. The texture is disordered and nonhomogeneous (bioturbation). Sorting is on the whole absent, but within the limits of tracks and nodules the material may be granulometrically homogeneous. Glauconite occurs.

3. Sediments that are still coarser; pteropodal-foraminiferal and polydetrital. Some of these are distinguished from the preceding only by the large admixture of pteropods, in others, in addition, many types of detritus (mollusks, spicule-skins, and corals). The fragment sizes range from fine silt to 2-3 mm and larger. Large, complete pelecypod and gastropod shells are encountered. Fragments of lithified mud (up to 1 cm in diameter) often occur; pellets are locally common.

4. Pelletal sediments, generally rather dark, marsh-green, and of diverse structure. They are comprised of oval pellets, in some cases fine (0.15-0.30 mm), in others coarser (up to 1-2 mm), noted visually. The pellets are formed of either pelletal carbonate-clay mud, or slurry-pelletal, more carbonate mud. Foraminifera (pelletal-foraminiferal sediment) or diverse shell detritus (polydetrital-pelletal mud) are present in different quantities. Remnants of unworked material are almost always preserved in the pelletal mass in the form of small lenses and irregular forms of portions.

All of the listed sediment types are connected by transitional varieties. These are the primary components of the sedimentary cover of the rift. They are, on the whole, hemipelagic formations.

In general, clear layering is not developed in the sediments, and they are either quite homogeneous, or material of varied granulometry, composition, and color (mottling) is distributed in them without order. Such a texture is primarily connected with the life activity of mud-dwellers, reworking and remixing the sediments. Relicts of fine layering are often preserved amid them.

Stratification. The dominant type of stratification is determined by alternation of pelletal muds with those that are "coarser," enriched in foraminifera, pteropods, and other

organic detritus. The sediment thickness of various structures generally varies within the limits 40-200 cm, but sometimes the entire revealed interval (3 m) is formed of homogeneous mud. In the sections, the transition from one sediment to another often occurs across a "mottled zone" from 40 to 150 cm in thickness, in which "bioturbational texture" is very clearly apparent. Apparently, this shows that the alternation of the sediments was accomplished through their interlayering.

Another, asymmetric-rhythmic type of stratification is observed much more seldom. As a rule, the rhythms are two-elemental. The first element (10-40 cm) is represented by foraminiferal, pteropod-foraminiferal, or organic polydetrital material, always with an admixture of pelite; sometimes the coarsest fragments are concentrated lower (gradational structure); the lower contact is sharp. The second element (30-150 cm) is formed of clay-coccolith mud with inclusions of coarser material (shelly slurry, fine shells of foraminifera). If one takes such inclusions as the remnants of interlayers, then second element represents layered sediment. Then the rhythm on the whole will correspond to the two lower intervals of the turbidite model (T_a , T_b). Three-element rhythms occurred in one of the test cores, in which the upper element was formed of finest carbonate-clay sediment (T_c); pteropod shells are sparsely distributed in it, while sponge accumulations are observed here and there. It is evident that the interval corresponds to "normal" hemipelagic sediment.

Main Structural Features of the Sedimentary Cover. From the above description it is clear that the rift deposits are rather uniform. Nonetheless, they experience specific changes both laterally and with age (Fig. 2).

In the central, depressional portion of the rift (depth 1200-1400 m), where most of the stations were concentrated, four packets are distinguished in the section. Their ages are estimated, respectively, as 10,000 (Holocene), 10,000-12,500, 12,500-15,000 years, and more ancient.

The first (upper) packet is formed of carbonate-clay and clay-carbonate muds, often reworked into pelletal sediment; intervals occur that are enriched by foraminifera, pteropods and other shelly detritus. Here and there are abundant sponges. The lower boundary is poorly defined in some cases, while in others it is sharp and rough, with channels deeply penetrating into the underlying sediment. The packet thickness generally varies within the limits 90-180 cm* seldom decreasing to 40-60 cm or increasing to 300-400 cm. The increase in the thickness occurs on the edges of the portions of the depression.

Redeposition of material here and there in the sections is established on the basis of absolute age dating.

The second packet is represented primarily by pelletal clay-carbonate muds that are finer and lighter, than those overlying. Shells of foraminifera and pteropods, and in places many sponges, are arranged in the deposits. The thickness varies from 70-180 cm, seldom falling to 50 cm.

The third packet resembles the second, but the sediment is still finer; the quantity of foraminifera and pteropods decreased, but sponges are abundant, particularly in the lower portion of the section. The appearance of polymict terrigenous silt (up to 25%) is characteristic, amid which are many rounded carbonate grains. The presence of a terrigenous admixture distinguishes this packet from every remaining section, where as a rule terrigenous grains are very rare. The thickness varies from 40 to 160 cm. Boundaries of packets are poorly defined and it is difficult to distinguish them from underlying deposits.

The fourth (lowest) packet resembles the preceding, but it contains somewhat more clay, and polymict silt is contained in it in insignificant quantity, although many sediments contain an admixture of well rounded carbonate grains. The apparent thickness varies from 40 to 120 cm.

On the whole we see that the section is rather uniform, although a tendency toward increased coarser material (shelly, pelletal) is rather clearly apparent in the upper part, as well as the appearance of an admixture of terrigenous silt in the middle (third packet).

These deposits are mostly distributed in the rift zone, and they may be considered as background. At the same time they undergo the alterations of nearby eruptive centers and tectonic terraces.

*If we neglect the extrusive field, where sediments are often absent.

On the basaltic uplifts, the regular sediment cover is insignificant and it does not develop universally, although its thickness sometimes reaches 70 cm and even more than 1 m. The sediments are relatively abundant here, and enriched by a variety of organic detritus, foraminifera, and pellets. They may be related to the upper packet and they are in general only slightly distinguished from the regular muds of this subdivision, but they often contain an admixture of basaltic fragments, particularly in the lower portion.

Atypical sediment occurs at one of the stations close to a tectonic uplift positioned in the axial portion of the rift zone. Its thickness is >200 cm, and in age it also belongs to the upper packet. The sediment is brown-green, extremely unsorted, and of chaotic structure. It is composed of a slurry-pelite (clay-carbonate) mass with a large quantity of fine and coarse organic detritus (pteropods and mollusks) and foraminifera. Basaltic gravels, pebbles (up to 8 cm), and sands are included in this sediment irregularly and without order. Somewhat coarser pebbles revealed serpulids and mollusks. Rare pebbles of recrystallized limestone containing basaltic sand are encountered together with the basaltic clasts. All this abundant material is carried away by uplift, and transported without order with the regular sediment. Such features may be connected with one of the types of gravitational transport through textural-structural features.

On the terraces which bound the rift (820-1000 m deep), the deposits are on the whole somewhat different, although they are also composed from the same sedimentary material as in the depressions. This is particularly noticeable in the upper portions of the section (Fig. 2, 4). The first packet here is preserved in thickness (sometimes up to 15 cm), it has a "coarser" composition, its lower contact is generally sharp and uneven, locally of the slump type; accumulations of coarse organic detritus are often observed at the base, pebbles of lithified sediment are often present. Lower lying deposits of the second packet are often strongly eroded completely washed away (Fig. 2 and 5), and the upper packet lies immediately on the third. This is well illustrated by both the absolute age dating, and the lithological data. Thus, for example, on the southern terrace (station 703), the 10-20-cm interval is dated numerically at 6320 ± 360 years, while the 50-60-cm interval is dated at $13,730 \pm 44$ years. A sharp and uneven contact is noted at a depth of 40 cm, below which the sediment is enriched by terrigenous silt, as is normal for the third packet of the section.

On most of the elevated portions of the terraces (depths <900 m), the deposits are on the whole coarser, nonuniformly enriched in various types of shelly detritus and foraminifera, and this relates not only to the Holocene, but also to the more ancient intervals.

All of the sections with rhythmic stratigraphic distribution in the terrace zone are complicated by faults. The conditions were most favorable here for the periodic redeposition of sediments and the washing away of relatively shallow water material into the region of regular mud distribution. Four to five rhythms are distinguished in the 5-6-m test cores. The thickness of the different rhythms varies from 55 cm to 1.7 m, seldom to 2.25 m. Their lower, coarse portion is always far thinner than the upper, finer portion. The rhythms of the various terraces are not correlateable among themselves. This indicates that their formation is connected not with sea level oscillations, but with locally arising material flows, stimulated by tectonic motions.

SOME FEATURES OF SEDIMENTATION

Deposits of the Tadzhur active rift zone are similar in their general outline to other low-spreading rifts of the "oceanic type." However its position in a narrow midcontinental basin (gulf), the relatively shallow water, and the lack of an intense display of volcanism superimpose a definite impression on the sedimentation.

As in open ocean rifts, the basic sediment forming components here are clay material and coccoliths; the admixture of tiny organogenic slime and principally pelagic foraminifera is constant. Moreover, as we have seen, various types of shelly detritus play a notable role in the sediments. The largest role belongs to the pteropods, which are present in the form of complete shells. Mollusks and other invertebrates play a smaller role. The granulometrically coarser sediments gravitated to the relatively shallow water (800-900 m) portions of the terraces and inner rift uplifts, and they may be utilized as specific "bathymetric calibrators" for paleoreconstructions.

Siliceous sponges are characteristic. They enrich many intervals of the section (Fig. 2) and are developed on rather extensive fields (Fig. 5). Apparently, the abundance of pteropods

and sponges distinguishes the considered territory from deeper water spreading zones of the open ocean.

The second feature of the deposits is their reduced character — these are green colored sediments, from light (increased carbonate) to dark; iron sulfides are constantly present, although in varying quantities. Oxidized yellow and red colored muds are absent. The deposits are noticeably distinct in this respect from the rift zones of the open ocean, for example, the Reykjanes ridge (Atlantic Ocean), where oxidized muds predominate [7]. Reduced sediments are also characteristic of other young depressions with oceanic crust, such as the Red Sea and the Gulf of California. This is explained by anomalies in the interchange with the waters of the open ocean [6].

The climatic environment influences the sedimentation in basins of the examined type. Evaporites or "black shales" may be formed in extreme conditions. In gulf-shaped rift basins which freely communicate with the ocean, the climate also influences the sedimentation, although not so sharply. Thus in the Gulf of Aden, which lies in an arid zone adjacent to large deserts, there is little terrigenous detrital material and it is almost completely of eolian origin. It was shown that the eolian admixture is concentrated in the 12-15 thousand year old sequence. This time corresponds to the aridization of the climate in lower latitudes.

We note that in the rift of the Reykjanes ridge, where there is also little terrigenous detrital material, its quantity increases on specific intervals. This is connected with epochs of cooling, introduction of the products of glacial erosion by icebergs, and the dispersion of fine glacial material by bottom currents [7].

Thus, it is seen that climatic fluctuations can be reflected in the sediments of rift zones of both midocean ridges and midcontinent gulfs.

One of the characteristic features of sedimentary processes in rift zones is the redistribution of sedimentary material; washing away from some areas and redeposition in others. This has been noted for the Reykjanes ridge, and it is well expressed in the Gulf of Aden. The lithological traces of redistribution are often not at all apparent, or weakly apparent due to the uniformity of the material. Only the systematic determination of the deposit's absolute age makes it possible to recognize the significance of this phenomenon.

Individual levels with sharply differing dates are often apparent on a background of regular age variations in the layers of the test core. Thus for example, the test core for station 790 (water depth 1040 m) had dates with the following values: the 80-90 cm interval: $8,670 \pm 170$ years, 130-140 cm: $13,790 \pm 310$ years, 160-170 cm: $30,870 \pm 1440$ years, 270-280 cm: $16,140 \pm 360$ years. It is evident that the third value indicates the introduction of more ancient material. Here and there are sediments of essentially different ages that are strongly "contiguous" in section, which indicates the washing away of a portion of deposits. This may be observed at station 696 (water depth 946 m) for example, where the 0-10 cm intervals are characterized by age values of 4980 ± 130 years, while the 50-60 cm intervals have values of $13,960 \pm 580$ years; a sharp change in the sediment occurs here at the 15 cm level here, accompanied by an uneven contact.

The "disordered" distribution of age datings sometimes stresses and features of rhythmic stratification: high values which conflict with the overall succession are here connected with coarse layers of the lower portion of the rhythms, that is: with sediments of gravitational flows.

It is natural that the processes of sediment redistribution are affected by the thickness of the deposits, which experiences noticeable variations. The largest accumulation occurred at the edges of depressions, whither material from the bordering terraces was carried. It comprises almost 20% of the depressional fill (data of V. M. Kuptsov). Erosional traces within the limits of the terraces are established particularly clearly for the beginning of the Holocene, when sediments of the second and partially of the third sequence were destroyed here.

The considered deposits pertain to a particular mid-continental rift zone, connected with the spreading and appearance of oceanic crust. In its physical-geographic relation, the rift belongs to the gulf, which apparently reflects the specific (young) developmental stage of an ensimatic (oceanic) basin. This structural and geographic position has been expressed in the sedimentation, although many of its features have already acquired similarity with sedimentation in the rifts of mid-ocean ridges. The similarity is determined by the unique

character of tectonic development (spreading and fault dislocation), magmatism and proximity to the derivation of the source of sedimentary material.

Moreover, in the relatively shallow water of mid-continental rift zones, including among them the Tadzhur rift, sediment formation possesses definite specific properties, expressed as follows.

The primary background sediments are hemipelagic sediments of intermediate depths (<2000 m). Climate is the paramount influence on their composition. In an arid zone (Gulf of Aden, Red Sea), in spite of the proximity to dry land, the deposits are strongly depleted in detrital terrigenous material, and it is principally of eolian origin. Here, as we have seen, lime-clay and clay-lime sediments (marls) predominate, corresponding to silt-pelite, and sometimes fine sand in granulometry. On the whole they are rather similar to the background sediments of many oceanic rift (spreading) zones, but the remnants of pteropods, mollusks, and other invertebrates, and sometimes abundant sponges, have a larger value in them. Radiolaria and diatoms play an insignificant role. In a humid zone (the Gulf of California) on the other hand, the essential components of sediments are terrigenous clastics supplied by rivers and biogenic silica (principally diatomaceous). Biogenic carbonate material is also sporadically present in small quantity.

Reduced sediments develop in the considered rift type (as distinct from oceanic rifts). This is determined by the anomalies in the interchange of the water masses of gulfs and the open ocean.

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IRON-MANGANESE NODULES AND CRUSTS FROM THE NORTHWESTERN PORTION
OF THE PACIFIC OCEAN

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UDC 552.124.4:552.2(265)

Textural-structural, mineralogical, and chemical investigations were conducted on iron-manganese nodules and crusts from the Shatsky and Hess rises and the Emperor fracture zone. It is shown that the studied nodules and crusts are similar in their internal structure and chemical and mineral composition. Based on the data we obtained, nodules which are depleted in manganese with low Cu and Ni content are principally composed of vernadite and weakly recrystallized iron hydroxides.

Iron-manganese nodules, a prospective mineral raw material of the future, have long attracted the attention of investigators. The wide distribution of nodules across the Pacific Ocean also caused their better study. The most detailed investigations of iron-manganese nodules have been carried out in the near-equatorial portion of the Pacific Ocean [3, 5, 13, 19, 20, etc.]. In recent years, serious consideration has been given to investigation of nodules in the southern portion of the Pacific Ocean [15, 16]. Until now, however, the nodules of the northern portion of the Pacific Ocean have been little studied. In the present article we examine for the first time the results of textural-structural and chemical-mineralogical investigations of crusts and nodules from the Shatsky and Hess rises and the Emperor fracture zone, which were performed on the 21st and 23rd trips of the NIS (Scientific-Research Station) Dmitrii Mendeleev.

Method of Investigation. Investigation into nodules and crusts were conducted by complex methods: optical, chemical, radiographic, and microprobe.

Polished thin sections of nodules were prepared by specialized methods without heating: varnish impregnation at room temperature and fastening in epoxy resin. Application of this method is connected with the fact that the ore material of the nodules is composed of slightly stable hydrous manganese minerals, and their heating leads to the withdrawal of molecular water and the disintegration of the structure [17].

Observation and microphotography of polished thin sections in reflected light was conducted for the study of the internal structure and mineral composition of the nodules and crusts. Laminar study of ore material by x-ray diffractometric analysis (DRON-1, $\text{CuK}\alpha$ -radiation, nickel filter, at 40 kV and 24 mA) was carried out by one of the authors of this article in the crystallography laboratory of the geologic faculty of Moscow State University (MSU). Microprobe study of different ore layers was carried out by Yu. S. Borodaevii on an x-ray spectral microanalyzer (JMA-5) at the field investigations department of the geological faculty of MSU. Only semiquantitative analysis was accomplished, since the water contained in the investigated minerals was not determined in the present apparatus, and it did not permit the performance of a complete quantitative analysis.

Determination of the chemical composition of the nodules was conducted at the Oceanological Institute of the Academy of Sciences of the USSR. Generally, an intermediate nodule specimen was analyzed (without core), while in the large, coarsely layered nodules the inner and outer ore coating were analyzed. The nodule samples selected for chemical analysis were dried at temperatures of 100°C, and then pulverized. Determination of the gross Fe, Mn, Co, Ni, and Cu content was carried out by the atomic-absorption method, while the colorimetric chemical method was used for Ti and for controlling Fe and Mn. Atomic-absorption analyses were performed by V. N. Gordeevii on the "Saturn" type of spectrophotometer, while the chemical analyses were performed by N. P. Tolmacheva.

Oceanological Institute, Academy of Sciences of the USSR. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 26-34, May-June, 1987. Original article submitted January 1, 1985.

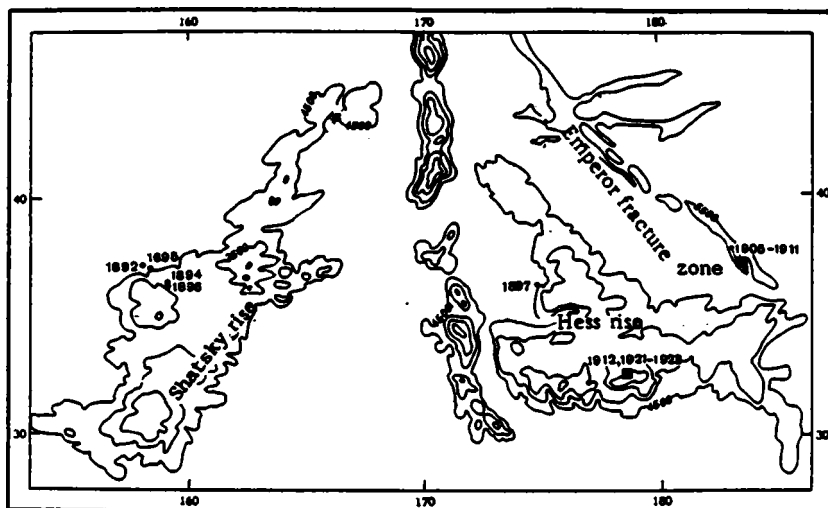


Fig. 1. Map of station positions.

Shatsky Rise. Geological efforts were conducted on a section across the northern slope of the central dome of the Shatsky elevation, at depths from 4900 to 3380 m. On the lower, gently sloping portion of the slope (Fig. 1, station 1892) at depths of 4600-4900 m, nodules of various morphological shape (oval-bulbous shaped, slabby, and intergrown) ranging in size from 1.5 to 10 cm, generally 3-5 cm, and crusts of nodular formation were brought up by dredge. The overwhelming majority of the nodules from the surface are covered by multiple thin overgrowths (secondary concretions). Pumice fragments in different degrees of argillization, and rarely slabs of compacted clay serve as cores of the nodules.

On the steep scarp of the slope's middle portion (Fig. 1, stations 1695, 1894) at depths of 3800-4300 m, oval-bulbous and rarely ellipsoidal nodules occur, in sizes from 1 to 12 cm, as well as fragments of pumice, blocks of clay and hyaloclastics covered by thin ore crusts ranging from fractions of millimeters to 1 cm. Argillized pumice and dense lumpy clay serve as the cores of the coarse nodules. These are often almost completely replaced by hydroxides fragments of ancient ore crusts, and rarely basalt and hyaloclastics.

On the upper portion of the slope at depths from 3880-3380 (station 1896) nodules were dredged up, in addition to fragments of ancient ore crusts ranging from 3 to 11 cm in thickness (with all sides covered by films of new portions of hydroxides), and blocks of basalt with ore crusts 2-4 cm in thickness.

The nodules are spherical/globular (5-10 cm), ellipsoidal, oval-flattened and slabby (5-12 cm). Fragments of ancient nodules, basalt, clay pellets, tuffs, and tuffobreccias serve as their cores. The majority of cores are completely replaced by ore material.

The ore coatings of the coarse nodules from stations 1894, 1695, and 1892 have similar internal structure (Fig. 2a).

Hess Rise. Nodules and ore crusts were detected on the western (steep) and southern slopes within the limits of the Hess rise.

On the western slope (station 1897) occur primarily coarse (more than 7 cm in diameter), spherical, ellipsoidal, and multiple cored oval-bulbous appearing nodules, lumps of hyaloclastics and dense zeolithized clays with thick ore crusts (up to 5-6 cm on the upper portions of the blocks). The nodules are coarsely layered with dense inner and friable outer ore coatings separated by interlayers of clay materials. Nodule fragments from earlier generations, blocks of zeolitized clay replaced to various degree by hydroxides, and often pumice (in the small nodules) serve as nodule cores.

Dredging was carried out on the rise's southern slope at depths from 4600 to 1850 m. At the foot of the slope, at depths of 4000-4600 m, fine discoidal nodules and their intergrowths and fragments of pumice with thin (2-3 mm) oxide crusts occur.

Fragments of spherical and pillow lavas, blocks of hyaloclastic and basaltic breccias, sometimes phosphoritized [2], fragments of phosphorites and phosphoritized limestones with ore films and crusts (thickness from 1 mm to 12.5 cm), and fragments of dense ancient ore

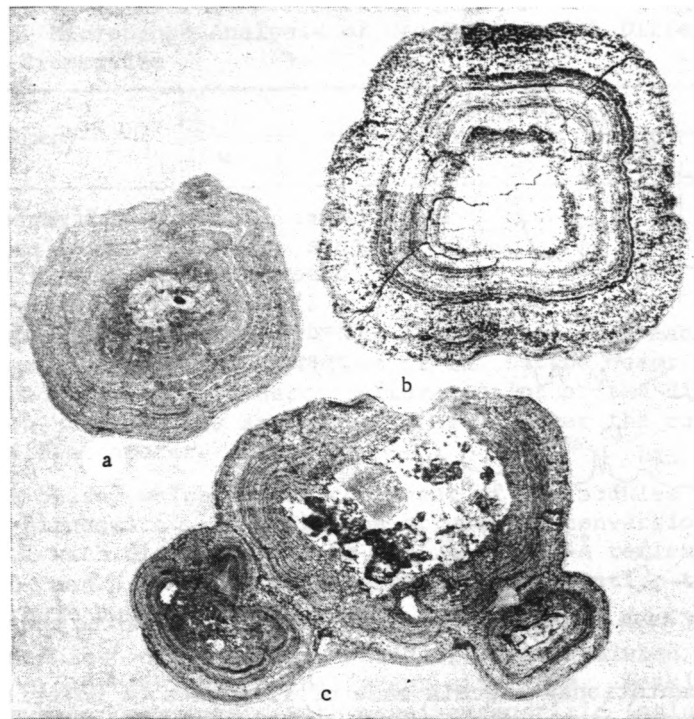


Fig. 2. Internal structure of nodules, polished thin sections. a) station 1892, $\times 0.9$; b) station 1896, $\times 1.0$; c) station 1909, $\times 0.8$.

crusts are detected on the middle and upper portions of the slope at depths ranging from 3750 to 1850 m. The maximum values and variations in the thickness of the ore crusts were noted on the upper part of the slope (station 1923).

The sharp variations in the thickness of the ore crusts on the surface of magmatic and sedimentary rocks are connected with multiple tectonic crushing of the southern portion of the Hess rise, which is accompanied by brecciation of the rocks and crusts. The polished fracture surfaces of the ancient ore crusts and the presence of slip reflection on samples of the native rocks are indications of the tectonic nature of this process.

Emperor Fracture Zone. Geological efforts on the 23rd trip of *NIS Dmitrii Mendeleev* were carried out over a transverse section of the southern portion of the fracture. Six stations were created in all. Dredging was carried out at four stations, and test cores of the sediments were obtained at two stations. Judging by the materials of the geological investigation, nodules are absent on the floor of the fracture ravine, which is covered by silica-clay hemipelagic muds. Nodules and ore crusts occur on the steep ravine slopes, which are practically bare of sediments, and on the sediment surface of the elevated northeast fracture block.

The exposed surface of the native rocks on the ravine slope is covered by rather thick (5-8 cm) ore crusts. Nodules occur in the west between projections of the cliffs and blocky collapses.

On the upper portion of the northeastern slope at depths from 5600-5700 m (station 1905) occur fine botryoidal appearing and intergrown nodules. Fragments of basalt, tectonobreccia, and rarely pumice serve as their cores. Similar nodules are also detected in the upper portions of the southwestern slope at depths from 4750-5000 m (station 1911). Coarse (>5 cm in diameter) spherical and ellipsoidal nodules with bulbous surfaces are also uplifted here. Fragments of basalt, tuff, dolerite, and compacted clays are detected in the nodule cores.

Principally coarse (5-10 cm) ellipsoidal, spherical, sometimes intergrown, rarely slabby nodules, and blocks of basalt and hyaloclastic breccia with ore crusts 2-5 cm in thickness are developed lower on the slope, at depths from 5600-6100 m (station 1909). Fragments of basalt, dolerite, slabs of hyaloclastics, silicon, and zeolitized clay occur in the nodule cores. The fine nodules do not contain clearly individual cores. The coarse nodules of the

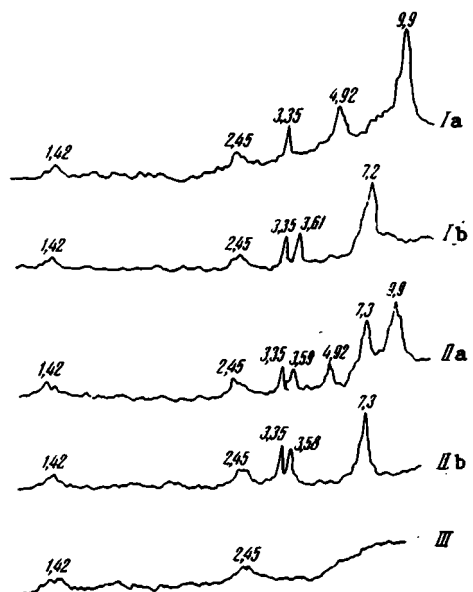


Fig. 3. X-ray diffractometric curves for ore material of nodules and crusts. I) buserite-1; II) buserite-1 + birnessite; III) vernadite + weakly recrystallized iron hydroxides (a, b: before and after heating, respectively).

Emperor fracture zone have a coarse-layered structure, similar to the nodules of the Shatsky and Hess rises.

A block of sedimentational breccia made of fragments of dolerites and gabbros, with a surface covered by an ore crust with asymmetric thickness (6 cm on the upper surface and millimeters on the lower), was dredged up from the lower portion of the southwestern slope of the fracture ravine at depths from 6800-7300 m (station 1907).

Internal Structure and Mineral Composition of Nodules and Crusts. Fine botryoidal-appearing and intergrown nodules that are generally fragile with a finely concentric-layered structure of ore coatings occur relatively rarely in the investigated area. Coarse nodules of the Shatsky and Hess rises and the slopes of the Emperor fracture zone are similar in their structure. These are coarsely layered nodules with dense concentric-layered internal (near-core) zones and friable, radially dendritic (columnar) outer coatings which are enriched by detrital-clay material (Fig. 2a-c). The concentric-layered nodule structure is caused by alternation of dark clay interlayers with ore layers which are distinguished in structure and optical properties.

Layers of ore material with low reflectivity are isotropic in crossed nichols, while those with higher reflectivity are characterized by anisotropy, manifested to different degrees dependent on the layer thickness. With increased thickness, the anisotropy of the ore material is intensified. This is evidently caused by the consolidation of the individual grains of the minerals which compose it.

Ore layers with different reflectivity are distinguished by mineral and chemical composition. X-ray diffractograms of samples selected from isotropic layers have two diffuse reflections, which are characteristic of vernadite ($\delta\text{-MnO}_2$): 2.45 and 1.42 Å (Fig. 3, III). Semi-quantitative microprobe analysis (Table 1) of the isotropic layers showed the presence of significant quantities of Mn and Fe in them. It is probable that the ore material of these layers is represented by thin intergrowths of weakly recrystallized hydroxides of Mn and Fe [10].

Microprobe and radiographic investigations of the anisotropic layers with high reflectivity show that they consist of either a 10-Å manganese phase (see Fig. 3, I), or a mixture of it with birnessite (Fig. 3, II, Table 1). It was considered earlier that a magnanese mineral with the following set of reflexes: 9.9, 4.92, 2.45, and 1.42 Å, relates to todorokite or 10 Å manganite in analogy with the phases synthesized by Buser and Gruter [12]. However, recent work by Chukhrova et al. [8, 9] and several foreign investigators [11] showed such manganese minerals as asbolan, asbolan-buserite, buserite-1, and buserite-2 have this set of interplanar spacings. The different behavior of the manganese minerals for low temperature heating are features of all five 10-Å manganese phases. Buserite-1 is the least stable under this influence. Weak heating transforms it into birnessite. As was shown in [8], this is connected with features of the structure of this mineral. In distinction from buserite-1, disappearance of the 10-Å peak and appearance of a 7-Å reflex does not occur in todorokite,

TABLE 1. Microprobe Analysis of Ore Layers with Different Optical Properties

Property	Component, %					
	Mn	Fe	Cu	Co	Ca	Si
Low reflectivity isotropic	12,4	10,5	0,14	0,13	6,1	0,5
High reflectivity, anisotropic	30,1	0,5	1,15	0,06	5,2	0,0n

asbolan, asbolan-buserite, and buserite-2. These features of 10-Å manganese minerals make it possible to diagnose them more precisely by means of the method described in article [6]. The essence of this method is described here: after receipt of the diffractogram from a selected polished section, the samples are heated to 100°C over the course of 1 h and then rephotographed in the diffractometer.

Heating of the 10-Å phase, which is the component of the nodules we investigated, led to its transformation into birnessite. An analogous structural conversion was also observed for a mixture of 10-Å mineral with birnessite: the 9.9- and 4.92-Å reflexes disappeared, while the intensity of the 7.3- and 3.59-Å peaks increased. Consequently, the 10-Å manganese phase of the anisotropic layers is buserite-1.

The layers of the nodules' ore coatings, which are distinguished by mineral and chemical composition and optical properties, have a different structure. Weakly recrystallized hydroxides of Mn (vernadite) and Fe form layers with massive-dendritic (columnar) structure. The space between dendrites is filled in by coating-clay material. The layer thickness varies from 0.3 to 3 mm.

The massive-dendritic layers are interlayered with thin (0.1-0.3 mm) colloform buserite interlayers (Fig. 4). They extend around the entire core portion of nodule without interruption and seem like marker horizons in the layers of the ore coating, indicating changes in the conditions of ore material accumulation.

Two essentially manganese interlayers of buserite-birnessite composition, with massive (Fig. 5) or skeletal-dendritic structure (thickness up to 3 mm), are detected in the inner zone of the coarse nodules.

As result of x-ray diffractometric analysis, the ore material of these layers is composed of a mixture of buserite-1 with birnessite, while the contribution of the birnessitic component is increased in the massive layers. This may be tentatively explained by the diagenetic transformation of manganese hydroxides. From the data of microprobe investigations, the manganese buseritic and buseritic-birnessitic layers are substantially enriched in copper (Table 1).

In distinction from the nodules, the ore crusts of the northwestern portion of the Pacific Ocean, which cover outcrops of the native rocks, have a rather single-form massive-dendritic (columnar) structure and are rather homogeneous in mineral composition. The ore material of the dendrites is characterized by low reflectivity and isotropy in crossed nicols. From the results of x-ray diffractometric (Fig. 3, III) and microprobe analyses, it is comprises of thin intergrowths of weakly recrystallized iron hydroxides with vernadite.

Chemical Composition of Nodules. The nodules of the Shatsky and Hess rises and the Emperor fracture zone are approximately the same (Table 2) in their gross content of Mn, Fe, Ni, Co, and Cu, and they are on the whole similar in their content of these elements to nodules from miopelagic clays of the northern portion of the Pacific Ocean [3, 19]. In Mn and Fe content and in the magnitude of the Mn/Fe ratios (from 0.49 to 2.05, generally less than 1.3) these are manganese-iron and iron-manganese nodules, with average values of almost equal Mn and Fe content. E. G. Gurvich et al. present similar magnitudes of Mn/Fe (0.5-1.05) for the Shatsky rise and the Emperor fracture zone [1].

Nodules from the investigated region that are enriched in Fe, with a low Mn/Fe magnitude are also characterized by low magnitudes of Cu, Co, and Ni, with average values, respectively, of 0.19-0.31, 0.15-0.26, and 0.29-0.57. A tendency toward an interrelationship of Ni and Cu with Mn is noted, as well as a close correlation of the Mn/Fe magnitude with r , equal to 0.77 and 0.68 (for a 99% significance level). This is reflected in the growth of the Ni and Cu

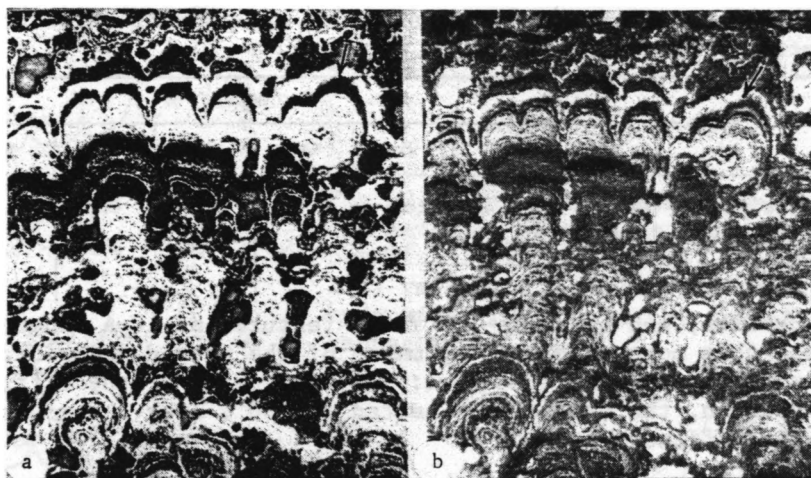


Fig. 4. Colloform structure of a layer which is anisotropic in crossed nicols (shown by arrow), formed of busserite-1, polished thin section, $\times 190$. a) parallel nicols; b) crossed nicols.

TABLE 2. Average Content (%) and Limits of Variation of Elements in Nodules and Ore Crusts

Content	Mn	Fe	Ti	Co	Ni	Cu	Mn/Fe	
Shatsky Rise (n = 13)								
Average	14,33	14,21	0,47	0,15	0,38	0,24	1,07	
Minimum	7,66	7,76	0,36	0,063	0,13	0,086	0,49	
Maximum	19,24	19,99	0,55	0,21	0,76	0,41	2,05	
Hess Rise								
Nodule Crusts (n=6)	Average	17,17	13,54	0,68	0,26	0,57	0,31	1,27
	Minimum	12,63	11,44	0,48	0,19	0,17	0,1	0,95
	Maximum	18,63	16,48	1,10	0,52	0,65	0,49	1,54
	Average	18,33	16,40	0,81	0,43	0,30	0,09	1,11
	Minimum	15,74	14,95	0,65	0,30	0,19	0,035	0,95
	Maximum	22,26	17,22	0,88	0,61	0,39	0,15	1,30
Emperor Fracture Zone (n = 13)								
Average	15,19	14,44	0,52	0,19	0,29	0,22	1,02	
Minimum	11,89	12,1	0,19	0,10	0,14	0,085	0,76	
Maximum	17,88	17,29	0,77	0,27	0,46	0,43	1,25	

content with increased Mn/Fe value. Laminar analyses of coarse nodules from the Shatsky and Hess rises showed an increase in the value of Mn/Fe (due to the decreased Fe content) in the inner near-core coatings. The maximum values for the investigated region of Mn/Fe (1.5-2.05), and Ni (0.55-0.75%) and Cu (0.39-0.49%) content occur here.

The ore crusts of the Shatsky and Hess rises and the Emperor fracture zone are close to the nodules in their Mn and Fe content and in the magnitude of Mn/Fe (0.85-1.3, generally <1) (Table 2). The ore crusts of the upper slope portion of the Hess rise (in the region of Mt. Melish) at depths less than 2000 m are an exception, since the maximum (20-22.2%) magnitudes of Mn content occur here, for increased Fe values, with magnitudes of Mn/Fe equal to 1.27-1.30. In addition to Mn, the content of Co (0.55-0.61%) increases significantly in the crusts, and the Cu content falls (0.035-0.15%).

The maximum value of Co content is noted in nodules from underwater mountains of pelagic regions at depths less than 1500 m [3, 7, 14, 21]. As was noted in [3, 7], the Co content grows parallel to growth of Mn content, during which that Co in the form of Co^{4+} apparently enters into the structure of vernadite: $\delta\text{-MnO}_2$.

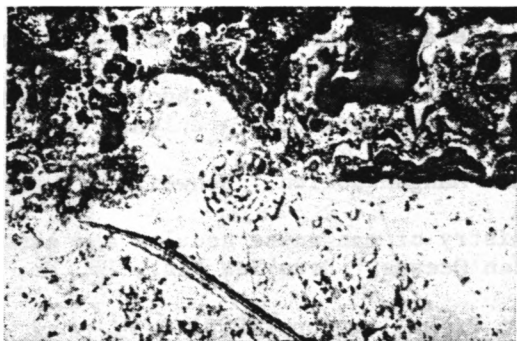


Fig. 5. Manganese interlayers with massive structure of ore material (white), composed of a mixture of birnessite and buserite-1, polished thin section, $\times 28$, parallel nicols.

Manganese-iron and iron-manganese nodules (with Mn/Fe generally < 1.5) of the northwestern portion of the Pacific Ocean are similar in structure and in chemical and mineral composition (they are principally composed of vernadite and weakly recrystallized Fe hydroxides) to the ore crusts from the surface of the native rocks, which are sedimentational in their genesis. They are formed principally from direct precipitation of Mn and Fe hydroxides from near-bottom water [4, 18]. The presence in the inner zones of the nodules of well expressed principally manganesic interlayers of buserite-birnessitic composition indicates the periodic alternation of sediment forming and ore forming conditions.

Their appearance in nodules may be connected with the change of sedimentation rates and near bottom currents, and the periodic burial of nodules under small (several millimeters) layers of semiliquid sediments. It is known that an increase in the Mn/Fe value in nodules from pelagic regions of the ocean is generally connected with the participation of the diagenetic processes of Mn remobilization in the upper sediment layer and its migration to the zone of nodule growth. Increase of sedimentation rates and the corresponding contents of buried organic material in the sediments may lead to Mn reduction, its segregation from Fe, and the formation of manganesic interlayers in the nodules. The presence of enriched Mn interlayers in coarse nodules from the Shatsky and Hess rises and the Emperor fracture zone, which are regions that are rather distant from one another, indicates periodic global changes in the conditions of ore formation.

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GENETIC TYPES OF CARBONATES IN THE LATE QUATERNARY SEDIMENTS OF THE CASPIAN SEA

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UDC 552.54:552.5(262.8)

In the article, we discuss the genetic types of carbonates in the Neocaspian and Late Volynsk sediments within various facies zones of the Caspian Sea. We establish that climatic changes and tectonic position influenced the process of carbonate accumulation.

A peculiarity distinguishing the process of carbonate accumulation in the Caspian Sea from other inland basins is the wide variety of types of carbonates in the sediments due to different sources of sediment. Investigators of the Caspian Sea did not immediately make note of the different types of carbonates present [1-7]. It has been during investigations primarily concerned with the modern deposits that the chemical compositions of the carbonates composing the sediments have been determined, the composition and structure of the oolites and sedimentary rinds studied, and the mineralogical and morphological types of carbonates given consideration.

The data which we collected on the distribution and types of segregation of carbonates in Recent, Neocaspian and Late Khvalynsk sediments which accumulated over the entire cycle of the latest glaciation (involving significantly contrasting conditions of sediment accumulation) allowed us to distinguish and characterize the various types of carbonates and to trace their

Moscow State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 35-43, May-June, 1987. Original article submitted March 24, 1986.

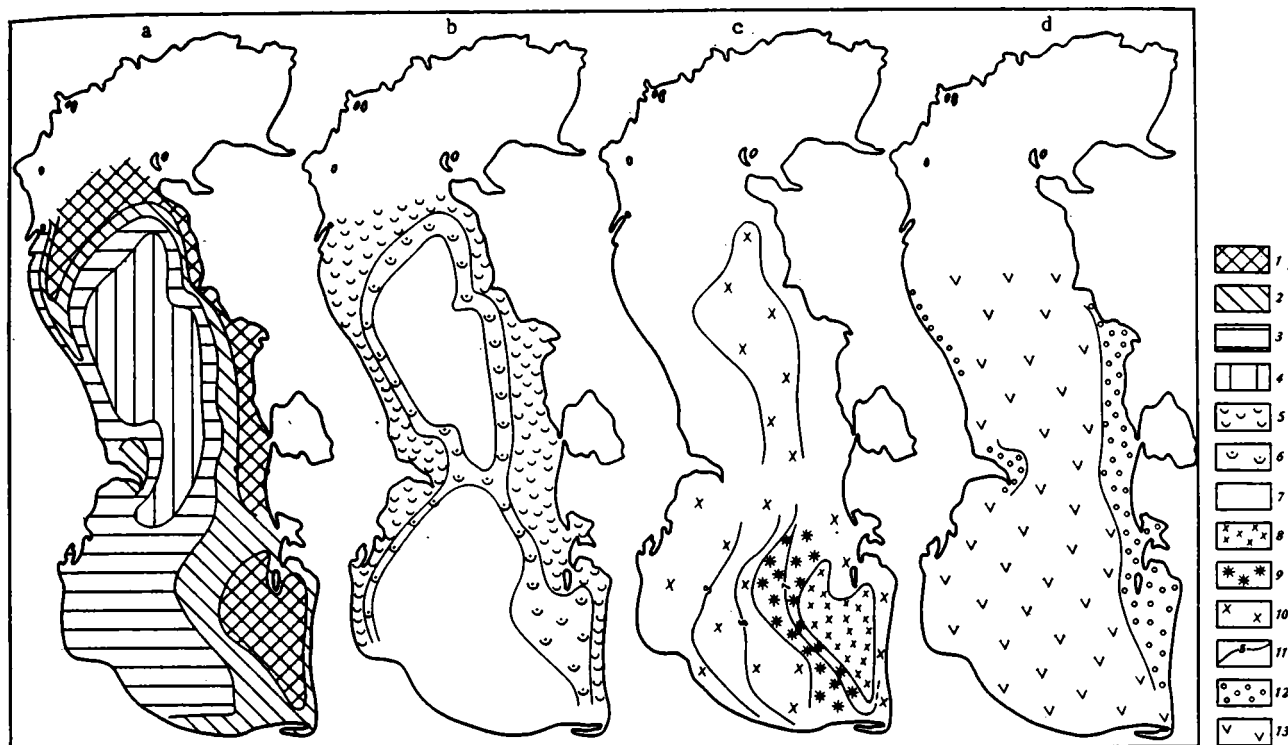


Fig. 1. Content of CaCO_3 , (a) and distribution of genetic types within the Caspian Sea (b-d) in Neocaspian sediments (b: biogenic, c: sedimentary chemogenic, d: same, diagenetic). 1-4) CaCO_3 content, %: 1) >50; 2) 30-50; 3) 15-30; 4) <15; 5-7) biogenic carbonates; 5) predominance in coquinas (50-100% of total carbonate content); 6) present in terrigenous muds (10-50% of the total carbonates); 7) insignificant content (<10% of total carbonate content); 8-10) sedimentary chemogenic carbonates; 8) predominance in calcareous muds of the shelf (75-100% of total carbonate content); 9) predominance in calcareous-clayey muds (75-100% of total carbonate content); 10) presence in terrigenous muds (10-100% of total carbonate content); 11) magnesium content of calcite, %; 12, 13) diagenetic chemogenic carbonates; 12) oolites and lithifacts; 13) finely crystalline calcite (10-50% of total carbonate content).

distribution over the area of the basin and along the sedimentary section with the use of modern methods of investigation which are more solidly grounded than previous methods.

The results of a study of more than 100 cores of sediment taken from the principal facies zones of the Caspian Sea in its the middle and southern areas, along with published data on the Northern Caspian [6], served as the basis for this report. Except for determinations of CaCO_3 content, the mineral compositions of the carbonates, both in bulk samples of sediments and in individual granulometric fractions, were studied by x-ray methods. In all, approximately 200 diffractograms were obtained, and the principal granulometric fractions in 14 cores were studied. In order to identify the chemical compositions of the carbonates responsible for the x-ray patterns, we carried out chemical analyses of the carbonates in 2% hydrochloric-acid extracts from 30 samples. The morphology of the carbonate particles was studied using both the usual optical method and high-resolution SEM.

The original carbonate material entered the Caspian Sea in three ways: introduced along with river drift, introduced as a result of coastal abrasion, and carried in along with wind-blown dust. The rivers introduce approximately 35 million tons of dissolved carbonates and approximately 15 million tons of suspended material annually. It is difficult to estimate the quantity of carbonates introduced by the two other routes. It can be assumed that between 5 and 10 million tons of solid carbonates enter along with dust [2, 5, 6]; these carbonates enter predominantly from the eastern shore. Several million tons of carbonates are apparently deposited on the bottom as a result of abrasion.

The carbonates studied in this report turned up in various quantities within the sediments (Fig. 1a). The maximum concentrations of CaCO_3 were associated with deposits on the eastern

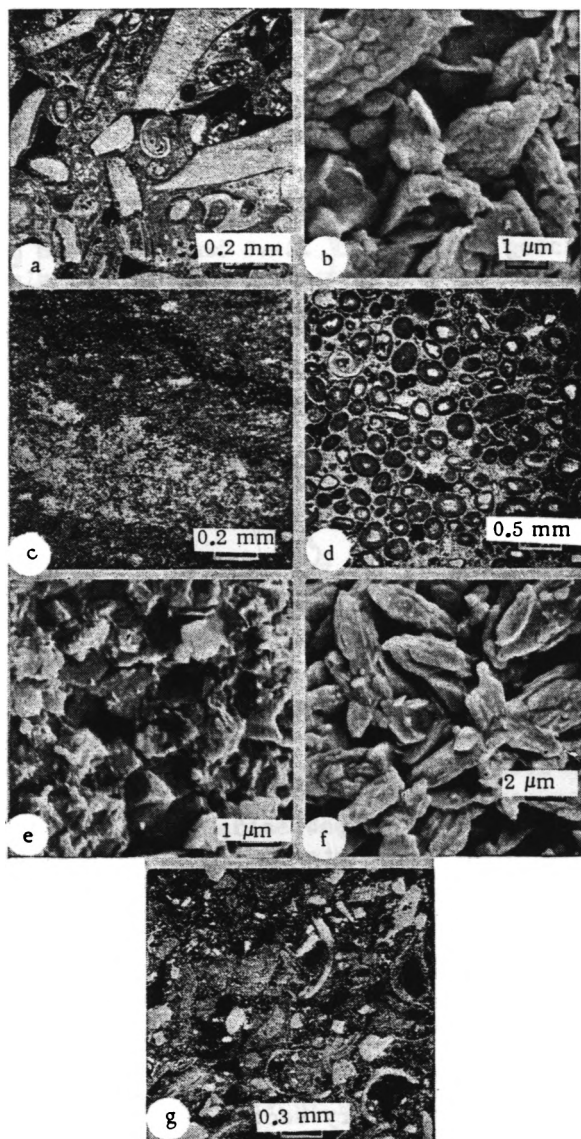


Fig. 2. Photomicrographs of carbonates. a) shell fragment of molluscs and gastropods (thin section, crossed Nichols, scale: 0.2 mm); b) crystals of magnesium calcite (SEM thin section, 1 μ m); c) interlayer of sedimentary carbonates in deep-water sediments (thin section, crossed Nichols, scale: 0.2 mm); d) overall appearance of oolite fragments; e) microstructure of oolites (SEM, scale: 1 μ m); f) diagenetic crystals of magnesium calcite in cement (SEM, scale: 2 μ m); g) fragments of calcareous rock among biogenic fragments (thin section, crossed Nichols, scale: 0.3 mm).

shelf of the Middle and Southern Caspian and, in part, to the western shelf. The CaCO_3 concentrations varied from 50 to 90% in the coquinas and fine-grained muds. The quantities of CaCO_3 were lower in the sands, silts, and silty muds of the western and northern shelf, usually varying between 10 and 50%. The fine-grained muds of the eastern half of the Southern Caspian can be distinguished in deep-water basins with elevated carbonate content, where these muds have CaCO_3 concentrations ranging from 30-50%. Over the rest of the basin's area, the CaCO_3 concentrations in the Neocaspian deposits rarely rise above 20% in the Middle Caspian and 30% in the South Caspian. The carbonate content in the sedimentary section varies in the following manner. As a rule, the carbonate content falls sharply in the Late Khvalynsk muds of the outer shelf. Coquinas and facies of Neocaspian age enriched in shelly material are replaced by slightly calcareous siltstones and silty-clayey muds. In deep-water deposits, the quantity of CaCO_3 begins to increase downwards along the section, reaching a maximum (30-40%) in the calcareous-clayey muds at the end of Late Khvalynsk times. The quantity of CaCO_3 then falls sharply (to 10% or less) in brown and reddish-brown clayey muds of Late Khvalynsk time synchronous with the maximum of the Ostashkovo glaciation (15,000-18,000 years ago).

Biogenic, chemogenic, and terrigenous types could be distinguished among the carbonates which we studied using genetic criteria.

The biogenic carbonates are the most widely distributed type in the sediments of the sea shelf (Fig. 1b). They are primarily represented by coquinas of benthic organisms; pelyceps, gastropods, ostracods, foraminifera, and the remains of calcareous algae are included (Fig. 2a).

According to our data and the data of other investigators, the Caspian molluscs construct their own shells from aragonite, the barnacles use calcite, and the ostracods, foraminifera, and calcareous algae use calcite with magnesium included. In individual instances, aragonite is transformed into calcite during recrystallization of the shells.

Biogenic carbonates are unequally distributed within the Late Khvalynsk sediments, both areally and along sections. Also, the variety of species within the remains decreases significantly from the shore to the deep-water region of the sea. In the upper horizons of the Neocaspian deposits, accumulations of mollusc shells forming coquinas have been noted over broad areas of the shelf in the eastern and northern portions of the basin. The biogenic carbonates are quite diverse within the range where mollusc shells are found. The maximum numbers of pelecypod varieties from the following genera occur here: *Didacna*, *Dreissena*, *Cardium*, *Monodacna*, *Abra*, and *Mytilaster*. Gastropods, ostracods, and benthic foraminifera are most abundant within this zone. It is very characteristic that the coarseness of the coquinas will decrease with increases of depth in the sea, with impoverishment of the species composition of the molluscs, and with smaller sizes of the species. The absolute and relative quantities of biogenic carbonates decrease in the areas where coquinas occur within the sands and silts of the shallow-water areas of the shelf and within the silty and silty-clayey muds of the outer shelf, although biogenic carbonates still remain the predominant type. The pelecypods in the finer-grained muds are represented by several species, but the numbers and species compositions of the ostracods and foraminifera are sharply restricted. Calcareous algae are distributed primarily within the shallows of the southeastern shelf, where their concentrations among the other carbonates sometimes become very significant.

As the total carbonate content decreases downwards along the section of Neocaspian and especially Late Khvalynsk deposits, the absolute amounts of biogenic carbonates and their importance among the other types decrease, most substantially in the western and northern portions of the Middle Caspian, where the coquinas are replaced by terrigenous sediments with admixtures of shells of benthic organisms and large quantities of fine-grained carbonates.

Biogenic remains occur extremely rarely in silty-clayey, clayey, and calcareous-clayey muds within the shelf. The types of carbonates under consideration are sharply subordinated to other types of carbonates in the deep-water depressions.

In general, a decrease in the amount of biogenic carbonates from 100 to less than 10% can be seen as one proceeds from coquinas to sands to silty muds to clayey muds.

A mineralogical analysis of the biogenic carbonates indicates that they consist of aragonite, just as in the source area for the biogenic remains. Calcite and magnesium calcite are present in significant quantities only in cases when foraminifera and calcareous algae play an important role in the sediments.

Chemogenic Carbonates. The Caspian Sea is one of the few basins in which chemogenic carbonate accumulation widely occurs. Several generations of chemogenic carbonates, both sedimentary and diagenetic, occur within the sediments. Supersaturation of the Caspian waters with carbonic acid [1] causes crystallization and precipitation of CaCO_3 to take place in the water by direct settling out on the bottom. Similar phenomena occur during the summer months in the shallows of several regions of the Southern Caspian (Lenkoran', the eastern shelf). The warm water has a milky color due to the carbonate material crystallizing within it.

When studied under a scanning electron microscope, the sedimentary carbonates from the chemogenic calcareous muds of the eastern shelf of the Southern Caspian appear as crystals of rhombic habit showing different degrees of perfection. Crystals with dimensions less than 0.005 mm predominate (Fig. 2b). They have a scaley texture on the edges apparently indicating incomplete crystallization of the particles. The carbonates of this type consist of high-magnesium calcite with an admixture of up to 8% MgCO_3 ($d_{100} = 3.01\text{--}3.015$ nm). The results of the x-ray analysis confirm the data from the chemical studies. According to the latter, the sedimentary carbonates include up to 3% MgO , which amounts to 5–8% MgCO_3 , recalculated for carbonate material *per se*.

Acicular "pancake" segregations of calcite possessing finely silty and coarsely pelitic dimensions can be seen in thin sections of material from the predelta fractions of the rivers (the Kura, Samur, and Ural rivers). In the opinion of Yu. P. Krustaleva et al [6], these carbonates are chemogenic and were formed in a zone of mixing for river and sea waters. In the clayey and silty fractions of sediments from the Northern Caspian, pelitomorphous chemogenic carbonates contain up to 15% MgCO_3 within a lattice of calcite (d_{100} up to 2.99 nm) [6].

Sedimentary carbonates are most abundant in the sediments of the Southern Caspian (Fig. 1c). Calcareous fine-grained mud composed of sedimentary carbonates and containing small admixtures of biogenic and terrigenous material are distributed over broad bottom areas of the eastern shelf and over the upper portion of the adjoining continental slope. The quantity of chemogenic carbonates within boundaries of these areas amounts to no more than 75% of the overall total. The sedimentary carbonates play a significant, although subordinate role, as fillers in coquinas and calcareous sands of the eastern shelf. The highly calcareous pelitic muds of the eastern half of the basin and the continental slope of the Southern Caspian contain these types of carbonates in quantities of up to 100%. It is interesting that the magnesium content of the calcite increases west to east from 3% up to 8% in the central area of calcareous sediments on the shelf.

The microcrystalline carbonates composing the thin (thicknesses of up to 0.5 mm) calcareous intercalations within the stratum of Neocaspian and Late Khvalynsk deposits in the calcareous and slightly calcareous clays and diatomaceous clays found over the remaining deep-water regions of the basin can be confidently classified as sedimentary (Fig. 2c). Probably, the fine-grained carbonates in the Neocaspian sediments of the shelf and western half of the Southern Caspian basin, composed of calcite, also have an initially chemogenic source.

In the Northern Caspian area, chemogenic carbonates constitute up to 5 or 10-20% of the total [6]. Here, the maximum amounts of chemogenic carbonates are found in the predelta regions of the Volga and Ural rivers and within the most fine-grained sands of the Ural trough. However, it is difficult to definitely judge whether the carbonates in this region are sedimentary or not.

In general, there is an increasingly important role for sedimentary carbonates starting with sands and coquinas (less than 10%) and proceeding to silty and clayey muds and further to pelitic (in terms of dimensions) highly calcareous clayey muds and calcareous muds in which sedimentary carbonates constitute up to 100% of the total. The highly calcareous sands and coquinas of the shallow areas of the Southern Caspian shelf, where the quantities of sedimentary carbonates are anomalously high, are exceptions to this sequence.

Aside from the sedimentary carbonates prevalent among the chemogenic varieties, diverse diagenetic and sedimentary-diagenetic chemogenic carbonates are present in the sediments of the Caspian Sea; these include: oolites, cementation rinds, lithifacts, and so forth (Fig. 1d).

The oolites in the sediments we studied are ball-shaped, ellipsoidal, or, more rarely, flat grains with 0.1-1 mm dimensions predominating. They have yellow, rust-brown, grey and black colors. The majority of the oolites form around particle fragments of various origins (Fig. 2d). In some varieties, the existence of a nucleus is clearly evident. As a rule, the body of the oolite consists of concentric layers of finely crystalline material. The number of layers varies from 1 to 10 or more. The thicknesses of the layers vary within a range of several hundredths of a millimeter. When there are large increases in thickness, it is evident that the individual layers consist of radially oriented crystals with dimensions of several micrometers and that the other layers are composed of thin, unoriented particles (Fig. 2d).

The x-ray study of the oolites showed that they were made, to an overwhelming degree, from crystals of magnesium calcite ($d_{100} = 30.1-3.015$ nm) with concentrations of $MgCO_3$ in the range of 5-8%. Aragonite can be identified on the diffractograms in some samples, but it most likely reflects the makeup of the biogenic nuclei.

According to our own data and the data in the literature [6, 7], the oolites are unequally distributed over the sea floor. They are most abundant in the sediments in the eastern shelf of the Southern Caspian, where they are represented by yellow and black varieties and lie in a belt bounded from the seaward side by the 35 m isobath and extending from the south to the north to the Apsheronsk step and further to the Middle Caspian. The oolites, being recent deposits, form sands with admixtures of biogenic remains here in places. In a number of cores they saturate the sediments to various degrees and occur both in coquinas and in sections of chemogenic muds. Such oolites are older and are characterized by black coloration.

A second region of active oolite formation is the western shelf of the Caspian Sea. Oolitic sands are distributed locally to a depth of 35 m within the boundaries of the Bakinsk archipelago and occur interfingering within the sedimentary section at a depth of approximately 30 m [3]. In the region of Mt. Derbent, recent oolites of rust-brown color constitute a

significant portion of the beaches and foreshore sands. It is quite probable that similar sands extend along the entire western shore of the Middle Caspian.

In the Northern Caspian, oolitic sands compose broad bottom areas around banks at depths of less than 10 m west from the Tyub-Karagan peninsula; they are represented by light-grey and yellow varieties to the west, yellow varieties within the center, and yellow varieties to the east [6].

Sparse grains of black oolites occur in sections of the deeper-water areas within shallow portions of the shelf and the upper zone of the continental slope.

Judging from the depositional features associated with the oolites in the sediments of the Caspian Sea, a large portion of the oolites were undoubtedly formed under conditions of an active hydrothermal regime at the surface of the water-sediment boundary via a complex sedimentary-diagenetic pathway. The oolitic sands should be included here, although they were deposited at a greater depth than in known regions of modern oolite formation [8]. Another portion of oolites present in the sedimentary section was possibly formed diagenetically.

Oolite formation in the Caspian Sea differs substantially from the analogous process in other regions of the World Ocean [8], where we have examples of oolite accumulation under predominantly tropical (modern and ancient) climatic conditions involving normal or hypersaline sea and ocean basins. As a rule, the oolites are distinguished by aragonitic compositions in these cases. In the Caspian Sea, they are formed in subtropical and temperate climate zones during lowered water salinity and are composed mainly of magnesium calcite and calcite [6, 7].

Diagenetic chemogenic carbonates have an active role in the cementation of the Late Quaternary deposits in the Caspian Sea; lithified rinds of various types are formed as a result. Cemented coquinas which are difficult to penetrate with corers are distributed over broad bottom areas on the eastern shelf of the Bakinsk archipelago. The process of their formation apparently begins with the formation of dense calcareous rinds in the shells of molluscs. The rinds are up to 2 mm thick and are composed of densely packed scalenohedrons of magnesium carbonate (5-8% MgCO_3) with dimensions of 0.001-0.005 mm. Intergrowth of the shells into lithofacts occurs further along, these lithofacts are several centimeters thick and armor the bottom surface.

Lithofacts consisting of cemented oolites are another widely occurring type of lithofact. These formations are pebble-sized. They occur in a bed of sediments on the eastern shelf of the Southern Caspian, in the coquinas of the eastern shelf of the Middle Caspian, within the Bakinsk archipelago, and in other localities. These lithofacts were formed by oolites cemented with white, fine-grained magnesium carbonate (Fig. 2f). The lithofacts are enveloped on the exterior by a yellowing rind of up to 2 mm thickness. This rind is composed of densely packed crystals of magnesium calcite. In the Neocaspian and Late Khvalynsk muds of the deep-water basin and the more coarsely-grained facies of the western shelf, a few diagenetic carbonates occur in the form of individual calcite rhombohedrons with dimensions of 0.005-0.05 mm, corrosion films around quartz grains, and different types of cement in sands and silts.

The terrigenous varieties of carbonates in the sediments are represented by detrital grains of calcareous rocks and carbonate minerals. They are mainly composed of calcite and dolomite. When studied microscopically, the terrigenous carbonates are visible as particles with various degrees of rounding, as well preserved rhombohedrons, as split crystals (Fig. 2g). Numerous grains with earthy tarnishes occur among the detrital grains of calcareous rock and carbonate minerals. A number of the fragments are finely-crystalline limestones. A cleavage plane can be seen in some of the particles. The carbonates being described here, in the majority of cases, sandy or silty dimensions and are distributed among other terrigenous fragments. In fine-grained muds, they coincide with coarse material concentrated in intercalations and are found extremely rarely in the groundmass.

Over the area of the basin, the maximum quantities of terrigenous carbonates are found in those regions where rivers discharge and calcareous rocks subjected to abrasion crop out at the shore. They are especially numerous in the sediments of the western and southern shelves, in particular, adjoining the deltas of the Samur, Terk, and Kur regions, next to the Mangyshlak peninsula, and so forth. The terrigenous-carbonate fraction, in the opinion of Yu. P. Khrustalev et al. [6], was brought in with wind-blown dust from the eastern desert regions. The quantity of terrigenous carbonates in the more fine-grained sediments decreases outward to the shelf zone. Their absolute amount varies little within the sedimentary section, although

their relative amount in the Khvalynsk deposits increases as a result of reductions in biogenic and chemogenic carbonates.

The largest quantities of terrigenous carbonates within the facies spectrum lie within the terrigenous sands and silty predelta areas of the rivers; these areas, as a whole, are distinguished by low carbonate content, but terrigenous carbonates make up more than 50% of all carbonates here. Their role in the sandy-silty sediments is important. These sediments are composed to a significant degree of material abraded from calcareous rocks; 75% or more of their total falls within the terrigenous-carbonate portion. Minimal concentrations of terrigenous carbonates are characteristic of the fine-grained clayey muds of the depressions. Consequently, the amount of terrigenous carbonates in the granulometric spectrum increases starting with coquinas and proceeding to sands and then decreases toward the crystals fractions.

The diversity of genetic types of carbonates in the Late Quaternary sediments of the Caspian Sea, along with the importance of individual types and their combinations within the boundaries of the actual regions, is controlled by features of the depositional environment and their changes over time. Basically, this involves the tectonic position and the climatic zonality associated with the supply of sedimentary material to the sea and the hydrochemistry of the sea's water.

In the western and southern regions of the basin adjoining the folded structures of the Caucasus and El'brus, from which an enormous quantity of detrital material emerges, the role of carbonates in the sediments is limited. Primarily terrigenous and biogenic types of carbonates accumulate here; the latter have appreciable importance in the shallows, where maximum productivity of molluscs exist. The relative quantities of terrigenous carbonates increase in sands and silts, while some amounts of chemogenic carbonate have been mixed in with terrigenous carbonates in the finer-grained deposits.

On the eastern and northern shelves, located within the platform and subplatform regions from which terrigenous material emerges in limited quantities due to the arid dryness, carbonates are prevalent in the sediments; it is the biogenic or chemogenic types of carbonates which are chiefly present. In the Middle Caspian, the chemogenic process is suppressed because of the presence of an upwelling of water not fully saturated with carbonic acid in this case and because biogenic carbonates compose the coquinas along the entire shelf. Under the favorable warming conditions in the Southern Caspian, the waters are supersaturated with carbonic acid. The wide occurrence of the chemogenic process here results in a prevalence of chemogenic carbonates in the sediments, except in the shallow-water zone, where biogenic carbonates predominate.

In the deep-water depressions in the sea, biogenic carbonates are extremely few and the sediments are distinguished by chemogenic carbonates (with some admixture of terrigenous carbonates).

Abrupt climatic changes affected both the quantitative and the qualitative aspects of carbonate build-up through the duration of Late Quaternary. The biogenic carbonates in the Late Khvalynsk sediments were allowed the smallest distribution during the time of the last glaciation; this limited distribution included biogenic carbonates occurring on the shelf and was caused by the less favorable living conditions for the producers, by the lower productivities of the producers, and by the restriction of the habitat zone for molluscs during the fall in sea level. The role of chemogenic carbonates was sharply subordinated at that time, with the exception of the role of chemogenic carbonates on the eastern shelf of the Southern Caspian. This was primarily as a result of the small flow of dissolved carbonates into the basin under conditions when chemical weathering was sharply suppressed by dryness (during abrupt aridization of the climate). The relative importance of terrigenous carbonates increased against this background. During the change in natural conditions from the ice age to the present time expressed in the rising sea level, the increasing temperature of the water, and the increasing stock of dissolved carbonates, favorable circumstances were created for biogenic and chemogenic precipitation of CaCO_3 , i.e., a situation came about typical of the present day as described above. It should be noted that the climatic oscillations in the fold-regions of the Caspian Sea are reflected to a large degree in the process of carbonate accumulation and carbonate combination and that the relative roles of carbonates of different origins are practically constant here. A restructuring process resulting in changes in the roles of individual genetic types of carbonates occurs in the platform regions.

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PHYSICOCHEMICAL SETTINGS OF URANYL ARSENATE ORE FORMATION

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UDC 553.495

The products of solution of synthesized uranyl arsenates (H-uranospinite — $10^{-43.58}$, zeunerite — $10^{-49.96}$, Ca-uranospinite — $10^{-45.76}$, and novacekite — $10^{-44.44}$) are determined in standard conditions; the free Gibbs energy of their formation is evaluated. It is shown that these minerals arise only in zones of oxidation of arsenic-containing endogenous uranium ores; the first of these minerals is formed in acid, the second in slightly acid, and the third in neutral and alkaline media. For novacekite to be formed, an additional magnesium source is required. Sodium uranospinite is formed in an extra-arid climate from high-salinity waters. A natural development of primary genuinely infiltrational accumulations of uranyl arsenates is not likely, in contrast to uranyl phosphates and uranyl vanadates.

In previous publications we have described the physicochemical settings of formation of certain important minerals of uranyl vanadate group (carnotite) and uranyl phosphates (autunite, torbernite, and H-autunite), which favor ore accumulations in the hypergenesis sphere [3, 4]. The present paper presents similar data for a different group of uranium micas: uranyl arsenates, which are an important mineral component of oxidation zones of endogenous uranium deposits.

"Uranyl arsenate" is a term covering a broad range of mineral species with the formula $Me_n(UO_2)_2(AsO_4)_2 \cdot xH_2O$. The more common representatives are uranospinite $Ca(UO_2)_2(AsO_4)_2 \cdot 10H_2O$, zeunerite $Cu(UO_2)_2(AsO_4)_2 \cdot 12H_2O$ and their analogs, which contain from six to eight molecules of crystallization water — metauranospinite and metazeunerite, respectively — less often tregerite $(UO_2)_3(AsO_4)_2 \cdot 12H_2O$, sodium uranospinite $Na_2(UO_2)_2(AsO_4)_2 \cdot 10H_2O$, hydrogen uranospinite $(H_3O)_2(UO_2)_2(AsO_4)_2 \cdot (6-10)H_2O$, novacekite $Mg(UO_2)_2(PO_4)_2 \cdot (10-12)H_2O$, abernatite $K_2(UO_2)_2 \cdot (AsO_4)_2 \cdot (8-10)H_2O$, and also barium variety (heinrichite or sandbergerite), zinc variety (lodevite), lead variety (helimondite), cobalt variety (kirchheimerite), iron variety (kalerite), bismuth variety (walgurgite), aluminum variety (paulite), hydroxide-calcium variety (arsenite-uranylite), hydroxide lead variety (hugelite), and other uranyl arsenates.

Arsenic-uranium micas are similar in their characteristics to phosphorus-uranium micas and often occur together with them. Data reported by Belova [1] and Chernikov [9] indicate

Ministry of Geology of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 44-54, May-June, 1987. Original article submitted April 3, 1986.

TABLE 1. Analytic Data on the Contents of Various Components in Solution ($-\log C_i$ mol/kg H_2O) After Dissolution of Synthetic Uranyl Arsenates (T 25°C, P 1 bar)

Mineral	pH (final)	Ionic strength of the solution	Time of stabilization, days	$\lg C_i$									
				U		Ca		Mg		Cu		As	
				I	II	I	II	I	II	I	II	I	II
H-uranospinite	2,11	0,01	17	2,95	2,96	—	—	—	—	—	—	2,97	2,96
	2,82	0,003	19	3,52	3,52	—	—	—	—	—	—	3,52	3,52
Ca-uranospinite	2,07	0,01	12	3,00	3,08	3,36	3,38	—	—	—	—	3,07	3,08
	2,97	0,0015	18	3,98	3,98	4,20	4,28	—	—	—	—	3,96	3,98
Novacekite	2,20	0,008	13	2,97	2,97	—	—	3,20	3,27	—	—	2,96	2,97
	2,81	0,003	15	3,55	3,55	—	—	3,85	3,85	—	—	3,56	3,85
Zeunerite	1,33	0,045	12	3,10	3,10	—	—	—	—	3,40	3,40	3,11	3,10
	2,03	0,01	14	3,85	3,85	—	—	—	—	4,14	4,15	3,86	3,85
	2,88	0,0025	15	4,76	4,80	—	—	—	—	5,0	5,10	4,80	4,80

Note: I = average measured; II = adopted.

TABLE 2. Results of the Calculation of Uranyl Arsenate Solubility Products

Mineral	pH	$\lg a_i$					pL^*	
		UO_2^{2+}	Ca^{2+}	Mg^{2+}	Cu^{2+}	AsO_4^{3-}	for given pH	adopted value
H-uranospinite	2,11	3,11	—	—	—	17,54	45,52	45,52±0,06
$(H_2O)_2(UO_2)_2(AsO_4)_2$	2,82	3,58	—	—	—	16,48	45,64	
Ca-uranospinite	2,07	3,25	3,55	—	—	17,88	45,81	45,76±0,05
$Ca(UO_2)_2(AsO_4)_2$	2,97	4,05	4,35	—	—	16,63	45,71	
Novacekite	2,20	3,14	—	3,44	—	17,41	44,54	44,44±0,11
$Mg(UO_2)_2(AsO_4)_2$	2,81	3,65	—	3,95	—	16,54	44,33	
Zeunerite	1,33	3,55	—	—	3,72	19,85	50,12	
	2,03	4,02	—	—	4,35	18,73	49,85	49,96±0,15
$Cu(UO_2)_2(AsO_4)_2$	2,88	4,90	—	—	5,20	17,46	49,92	

that they are widespread in oxidation zones of uranium deposits whose primary ores contain arsenides, arsenopyrite, arsenic-bearing pyrite, or authigenic arsenic. The oxidation of arsenides (schmaltite, rammelsbergite, nickeline, and others) is extremely rapid, much faster than with most sulfide minerals and especially pyrite [2, 13, 14]. As a result, the secondary minerals appear already in the first alteration stage of endogeneous uranium ores along with hydrated oxides and silicates of uranyl and before uranyl phosphates [1]. Most uranyl arsenates, however, arise at the same time as do phosphates in the second stage of oxidative process, during which the acidity of the medium rises. On the other hand, uranyl arsenates have a lesser tendency to form redeposited ore accumulations than uranyl phosphates; as one moves from the central parts of ore bodies to the perimeter, the former sometimes give way to the latter [1], suggesting a mineral zonality of secondary dispersion halos.

Chernikov [9] believes that in order for uranyl arsenates to accumulate — in contrast to uranyl phosphates — neither a high sulfidity of the initial substrate, nor a high acidity of the medium is necessary. Such accumulations may develop in any oxidative setting, given the source of uranium and arsenic; alkaline media are most favorable for their deposition.

For a reliable evaluation of the physicochemical formation settings of different-cation uranyl arsenates in the hypergenesis sphere, the values of their solubility products have to be known. Such data are available in reference literature [6] only for two mineral forms of this group: sodium uranospinite and its potassium analog (anhydrous variety of abernatite). The pL^* values of these compounds, based on experimental studies by Chukhlantsev and Sharova [10], are: for $Na_2(UO_2)_2 \cdot (AsO_4)_2$ — 43.74, for $K_2(UO_2)_2(AsO_4)_2$ — 45.2. The values $\Delta G^{\circ}f_{(298.15)}$ computed by us on the basis of recent coordinated thermodynamic constants* of these materials (disregarding crystallization water) are -951.64 and -963.48 kcal/mol.

In order to supplement these data, we have investigated the solubility of another four chemically pure uranyl arsenates: hydrogen uranospinite $(H_2O)_2(UO_2)_2(AsO_4)_2 \cdot 8H_2O$, its calcium analog $Ca(UO_2)_2(AsO_4)_2 \cdot 8H_2O$, novacekite $Mg(UO_2)_2(AsO_4)_2 \cdot 8H_2O$, and zeunerite $Cu(UO_2)_2(AsO_4)_2 \cdot 10H_2O$, obtained in standard conditions synthetically.

The methods of synthesis of hydrogen and calcium uranospinite have been described by Winkler [20] and Morse [17, 18]; zeunerite by Werter [19], Frondel [15], and other investigators. Novacekite, described by Frondel [16] as an arsenic analog of magnesian uranyl phosphate — saleite — was discovered in the USSR more than two decades later [8] and was synthesized for the first time by one of the present authors by acting with a 2% solution of magnesium chloride on synthetic H-uranospinite for 3 months; Ca-uranospinite has been synthesized similarly, substituting $CaCl_2$ for $MgCl_2$. H-uranospinite was synthesized by mixing 0.5 M solutions of uranyl nitrate and arsenic acid warmed to 60-70°C with a stoichiometric ratio of the agents. Zeunerite can be produced readily in standard conditions by pouring together into a container the solutions of uranyl nitrate, arsenic acid, and copper sulfate.

X-ray investigations in an RKU-114 unit with $FeK_{\alpha,\beta}$ radiation showed that all the uranyl arsenates synthesized are identical in their crystal structure to their natural prototypes.

The solubility of each of these uranyl arsenates, as well as previously studied uranyl vandates [4] and uranyl phosphates [3], has been studied by us in the acid region for two or three different pH values. Weighted amounts of minerals (200 mg) were covered with HCl solution

*The thermodynamic constants are borrowed here and hereafter from [6, 7].

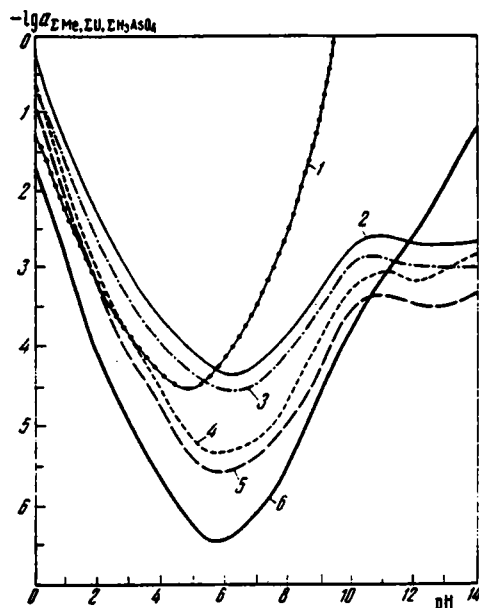


Fig. 1. Calculation curves of solubility of various uranyl arsenates vs. pH (25°C, 1 bar, $a_{\Sigma\text{CO}_2} = a_{\Sigma\text{SO}_2} = 10^{-2.5}$ mol/kg H₂O):

(1) H-uranospinite; (2) Na-uranospinite; (3) abernatite; (4) novacekite; (5) Ca-uranospinite; (6) zeunerite.

(200 ml) in different concentrations prepared from sulfuric acid of pure grade and a bidistillate. The dissolution was conducted in a polyethylene vessel with a thermostat at 25°C and regular manual stirring; after the solution settled, 5 ml was taken to determine the components of the initial mineral — U and As for H-uranospinite; U, As, and Ca for calcium uranospinite; U, As, and Mg for novacekite; and U, As, and Cu for zeunerite. Uranium was evaluated by the vanadotometric method; in the presence of copper it was first separated on silica gel. Cu, Mg, and As concentrations were measured with a POLIVAK E-2000 plasmatron. To monitor the measurements, Mg and Ca were additionally determined by the atomic absorption method, Cu by a polarographic, and U on a plasmatron. The mean of four measurements was taken as the final value.

The results of the measurements are given in Table 1. The determinations of molal concentrations of U and As for H- and Ca-uranospinite; U, As, and Mg for novacekite; and U, As, and Cu for zeunerite show a satisfactory match. In all experiments the plateau indicating equilibrium being achieved in the system appeared from the 12th to 20th days.

The analytic data were used to calculate the products of solubility of the four minerals. As in earlier studies, the activeness coefficients γ_i were computed with the Debye-Huckel formula [6], where a° for single-charge ions was set at 3.5 and for double-charged ions at 6.0.

The gross concentration of U in the water-salt system was determined by the sum of molalities of uranyl, its hydroxide complexes, and Cl-complexes:

$$C_{\Sigma\text{U}} = \frac{a_{\text{UO}_2^{2+}}}{\gamma_{\text{UO}_2^{2+}}} + \frac{a_{\text{UO}_2\text{Cl}^+}}{\gamma_{\text{UO}_2\text{Cl}^+}} + \frac{a_{\text{UO}_2\text{OH}^+}}{\gamma_{\text{UO}_2\text{OH}^+}} + \frac{a_{(\text{UO}_2)_2(\text{OH})_2^{2+}}}{\gamma_{(\text{UO}_2)_2(\text{OH})_2^{2+}}} + a_{\text{UO}_2\text{OH}_2^0}; \quad (1)$$

the gross concentrations of calcium, magnesium, and copper were estimated as the sums of molalities of like ions, their Cl-complexes (for Cu), and hydroxide complexes:

$$C_{\Sigma\text{Ca}} = \frac{a_{\text{Ca}^{2+}}}{\gamma_{\text{Ca}^{2+}}} + \frac{a_{\text{CaOH}^+}}{\gamma_{\text{CaOH}^+}}; \quad (2)$$

$$C_{\Sigma\text{Mg}} = \frac{a_{\text{Mg}^{2+}}}{\gamma_{\text{Mg}^{2+}}} + \frac{a_{\text{MgOH}^+}}{\gamma_{\text{MgOH}^+}}; \quad (3)$$

$$C_{\Sigma\text{Cu}} = \frac{a_{\text{Cu}^{2+}}}{\gamma_{\text{Cu}^{2+}}} + \frac{a_{\text{CuCl}^+}}{\gamma_{\text{CuCl}^+}} + \frac{a_{\text{CuOH}^+}}{\gamma_{\text{CuOH}^+}} + \frac{a_{\text{Cu}(\text{OH})_2^-}}{\gamma_{\text{Cu}(\text{OH})_2^-}} + \frac{a_{\text{Cu}(\text{OH})_4^{2-}}}{\gamma_{\text{Cu}(\text{OH})_4^{2-}}}; \quad (4)$$

the gross concentration of arsenic was defined as the sum of molalities of arsenic acid and its dissociates:

$$C_{\Sigma\text{As}} = a_{\text{H}_3\text{AsO}_4^0} + \frac{a_{\text{H}_2\text{AsO}_4^-}}{\gamma_{\text{H}_2\text{AsO}_4^-}} + \frac{a_{\text{HAsO}_4^{2-}}}{\gamma_{\text{HAsO}_4^{2-}}} + \frac{a_{\text{AsO}_4^{3-}}}{\gamma_{\text{AsO}_4^{3-}}}. \quad (5)$$

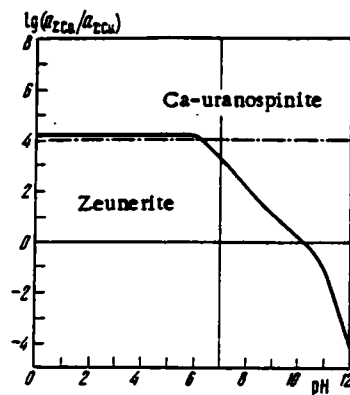


Fig. 2

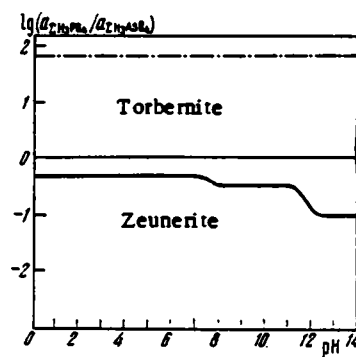


Fig. 3

Fig. 2. Correlation of Ca-uranospinite-zeunerite equilibrium line with pH ($a_{\sum \text{CO}_2} = a_{\sum \text{SO}_4} = 10^{-2.5}$ mol/kg H₂O). Dash-dot line represents the ratio of mean Ca and Cu contents in ground-water (data of S. L. Shvartsev).

Fig. 3. Torbernite-zeunerite equilibrium line vs. pH ($a_{\sum \text{CO}_2} = a_{\sum \text{SO}_4} = 10^{-2.5}$ mol/kg H₂O). Dash-dot line represents the ratio of mean P and As contents in groundwater (data of S. L. Shvartsev [11]).

Since the solubility of uranyl arsenates was studied in the acid region, we can disregard the last three terms of (1), the second terms of (2) and (3), the last three terms of (4), and the last two terms of (5) because of the smallness of these variables. Making use of the dissociation constants of arsenic acid, the constants of cation hydrolysis and complex formation calculated with [6], we then obtain

$$a_{\text{UO}_2^{2+}} = C_{\sum \text{U}} \frac{\gamma_{\text{UO}_2^{2+}} \gamma_{\text{UO}_2\text{Cl}^+}}{\gamma_{\text{UO}_2\text{Cl}^+} + a_{\text{H}^+} \cdot 10^{0.21}}; \quad a_{\text{Ca}^{2+}} = C_{\sum \text{Ca}} \gamma_{\text{Ca}^{2+}}; \quad a_{\text{Mg}^{2+}} = C_{\sum \text{Mg}} \gamma_{\text{Mg}^{2+}};$$

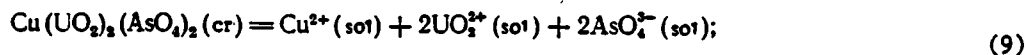
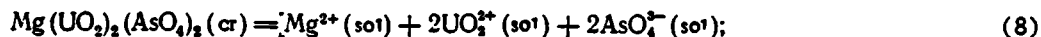
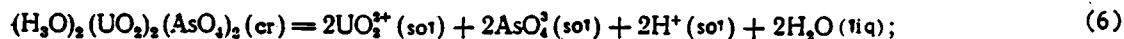
$$a_{\text{Cu}^{2+}} = C_{\sum \text{Cu}} \frac{\gamma_{\text{Cu}^{2+}} \gamma_{\text{CuCl}^+}}{\gamma_{\text{CuCl}^+} + a_{\text{H}^+} \cdot 10^{0.95}}; \quad a_{\text{AsO}_4^{3-}} = C_{\sum \text{As}} \frac{10^{-20.75} \gamma_{\text{H}_2\text{AsO}_4^-}}{a_{\text{H}^+}^3 \gamma_{\text{H}_2\text{PO}_4^-} + a_{\text{H}^+}^2 \cdot 10^{-2.26}}.$$

The solubility products of hydrogen uranospinite is found by multiplying squared activeness values of the ions H⁺, UO₂²⁺ and AsO₄³⁻ at the final pH value of the experiment, for calcium uranospinite by multiplying the activeness of Ca²⁺ and squared activeness of UO₂²⁺ and AsO₄³⁻; novacekite, the activeness of Mg²⁺ and squared activeness values of UO₂²⁺, AsO₄³⁻ and zeunerite, by multiplying the two latter squared values and the activeness of Cu²⁺.

The results of the calculations are given in Table 2.

The logarithms of solubility products for each of the minerals obtained with two different pH values (for zeunerite, three different pH values) are seen to differ by not more than in the first decimal place.

Taking for the average pL° of H-uranospinite 10^{-45.58}, Ca-uranospinite 10^{-45.76}, we can estimate the free Gibbs energy of the formation of these minerals with the equations of the reactions:



$\Delta G^{\circ}f_{(298.15)}(H_2O)(UO_2)_2(AsO_4)_2 = -843.35 (\pm 0.08) \text{ kcal/mol}$; $\Delta G^{\circ}f_{(298.15)} \cdot Ca(UO_2)_2(AsO_4)_2 = -961.34 (\pm 0.07) \text{ kcal/mol}$; $\Delta G^{\circ}f_{(298.15)} Mg(UO_2)_2 \cdot (AsO_4)_2 = -936.23 (\pm 0.15) \text{ kcal/mol}$; $\Delta G^{\circ}_{(298.15)} Cu(UO_2)_2(AsO_4)_2 = -819.35 (\pm 0.19) \text{ kcal/mol}$.

With n molecules of crystallization water included in the composition of each uranyl arsenate, the absolute value $\Delta G^{\circ}f_{(298.15)}$ of its formation will be increased by $56.69 n \text{ kcal/mol}$, respectively.

Figure 1 plots solubilities calculated from thermodynamic values of six uranyl arsenates vs. pH for activeness levels $\sum CO_2 = \sum SO_4 = 10^{-2.5} \text{ mol/kg H}_2O$, which corresponds to the natural subsurface hydrogeochemical systems in arid and semiarid provinces. The method of construction of these curves has been described in [3, 12, 14].

All uranyl arsenates exhibit two distinct solubility maxima (acid and alkaline) and are similar in that respect to uranyl phosphates [3]. There is thus no reason to contrast these two groups of uranium micas in the role of acidity of the environment for their formation [9]. As with uranyl phosphates, the solubility minimum of the minerals of this group for the common carbonate levels of groundwater corresponds to acidulous media (pH ~ 6.0); for hydrogen uranospinite it is shifted toward the acid region (pH ~ 5.0).

The solubility curves of sodium, potassium, calcium, and magnesium uranyl arsenates are similar, with the acid maximum being more pronounced than the alkaline maximum. The solubility curve of copper uranyl arsenate — zeunerite — is symmetrical. This mineral is more stable than the other four; in acid, quasineutral, and moderate alkaline settings it becomes highly soluble in ultraalkaline media due to formation of carbonate and hydroxide complex anions of Cu. The solubility curve of H-uranospinite is quite different, with an abrupt rise already in the slightly alkaline region; at pH > 8.5 this mineral is as soluble as at pH < 1.

Proceeding from these numeric characteristics, we will discuss the natural physical and chemical conditions conducive to the formation of the various minerals of the uranyl arsenate group. By solving the equilibrium equations of the individual pairs of these minerals the following has been determined.

Potassium uranyl arsenate (abernatite) gives way to its sodium analog (Na-uranospinite) when the molal concentration of Na^+ in the solution exceeds that of K^+ by more than a factor of 5.4. The mean Na content in groundwater in the hypergenesis sphere is 45.5 mg/liter and for K it is 4.5 mg/liter [11], i.e., the amount of sodium (in molal concentrations) is greater here than that of potassium by a factor 16.8; in groundwaters of the arid zone this predominance is even greater (by 19.8 times); in ocean water it attains a value of 45.5. Large additional potassium sources are thus required to enable the formation of abernatite; these sources could be potassium feldspar and mica decaying in an acid medium (with, for example, kaolinite replacement). For this mineral to be formed in the hypergenesis sphere the decay of rock-forming components is necessary, implying a high sulfidity of the substrate; otherwise, Na-uranospinite would be formed, all other conditions being equal.

Magnesium uranyl arsenate (novacekite) can compete with calcium uranospinite only if the activeness of Mg^{2+} ions is higher than that of Ca^{2+} by more than a factor of 21.4. The molal concentrations of these alkaline-earth elements in natural groundwaters, however, are either similar or with a slightly greater prevalence of Ca (according to Shvartsev [11] its concentration in groundwaters of an average salt composition is higher by a factor of 1.4 and in groundwater of the acid belt by a factor of 1.2). Novacekite, therefore, is a relatively scarce mineral; it would not be formed by the ordinary groundwater activity and is likely to be created only where high-magnesium rocks are decayed.

Based on the average contents in hypergenesis groundwaters reported by Shvartsev [11] for Na (45.5 mg/liter), Ca (43.9 mg/liter), and Cu (5.58 μ g/liter), one can conclude that with such "background" waters of the four principal minerals (H-uranospinite, zeunerite, Ca-uranospinite, and Na-uranospinite) the first will be formed at a pH of less than 4.0, the second in the interval 4.0–6.2, and the third at >6.2. Na-uranospinite cannot be formed from groundwater of this average composition at all. This means that when in oxidation zones hydrogen uranyl arsenate is replaced by copper uranyl arsenate and the latter by calcium modification, all other conditions being equal, this may be representative of a consecutive decline of the acidity of the mineral system with formation of the first mineral in highly acid, the second in slightly acid, and the third in neutral and alkaline environments.

As can be seen from Fig. 2, in an acid-near-neutral medium, calcium uranospinite is formed instead of zeunerite if Ca concentration in the solution exceeds the Cu concentration by more than $10^{4.1}$ times; in alkaline, substantially carbonate media ($\alpha_{\Sigma \text{CO}_2}$ close to $10^{-2.3}$ mol/kg H_2O), common in arid provinces, the Ca-uranospinite field progressively drives out the zeunerite field, and starting from pH 10 zeunerite is not formed even when Cu is predominant over Ca in the solution.

Calculations show that the equilibrium of sodium and calcium uranospinite is attained at a ratio of squared activeness value of Na^+ to that of Ca^{2+} equal to $10^{2.62}$. For average Ca contents in groundwaters of the hypergenesis sphere of 43.9 mg/liter (10^{-3} mol/kg H_2O) Na concentration in the solution ought to be 7.8 g/liter; for Ca 10^{-2} mol/kg H_2O , and 23 g/liter for Na (disregarding the effect of the ionic forces), i.e., high-salinity waters are necessary. This condition is fulfilled, for example, by ocean water, where the ratio $C_{\text{Na}^{+2}}/C_{\text{Ca}^{2+}}$ attains $10^{1.29}$. The occurrence of Na-uranospinite in oxidation zones of ore deposits thus may be an indicator of an extra-arid climate with intense evaporation of groundwaters and soil salinization that existed in the area in the past. One can arrive at a similar conclusion by considering the conditions of thermodynamic equilibrium between sodium uranospinite and zeunerite.

This is confirmed by mineralogic studies by Belova [1], who established that in subsurface parts of oxidation zones in some sulfide-uranium deposits there is an increase in the amount of Na-uranospinite which replaces first Ca-uranospinite and then zeunerite. The author rightly attributes this phenomenon to an abrupt aridization of the climate in the Neogene-Quaternary time, when the portion of the deposit was in a solonchak area with chlorite-sodium groundwater of a high salt concentration, typical for such areas; the young age of Na-uranospinite mineralization is also confirmed by radiologic data.

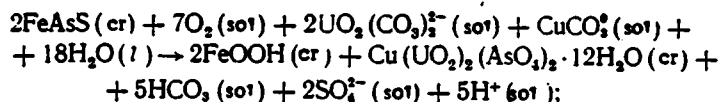
The formation of zeunerite, which is the frequent natural uranyl arsenate, according to calculations does not require a favorable Cu source in the rocks being oxidized or a heightened copper content of groundwater, contrary to the theory proposed by Chernikov [9]. This mineral can be formed in oxidation zones of As-containing uranium ores in a moderately acid region, as has been shown above, and in the presence of background levels of Cu in the hydrochemical environment. Uranyl arsenates containing alkaline-earths of Ca (uranospinite) or Mg (novacekite) appear as minerals of near-neutral or relatively alkaline media; in more acid settings, they are replaced by zeunerite, and in surroundings with high-salinity waters by Na-uranospinite or abernatite (in the case of an intense acid decomposition of potassium aluminosilicate rocks).

Calculations show that in humid provinces (tropical belt, permafrost areas, moderate climates, and mountain countries), where the ratio of the activeness levels of the ions of Ca^{2+} and Cu^{2+} in groundwaters is usually less than $10^{4.1}$, the principal uranyl arsenate to be formed in acidulous media must be zeunerite; in arid provinces, where the ratio of $C_{\text{Ca}^{2+}}/C_{\text{Cu}^{2+}}$ in groundwater is on the average $10^{4.32}$ [11], it should be calcium uranospinite. The zones of oxidation of arsenic-uranium deposits with a widespread zeunerite mineralization may thus be an indicator of humid conditions of hypergenesis; the presence of Ca-uranospinite would indicate arid conditions and of Na-uranospinite extra-arid climates.

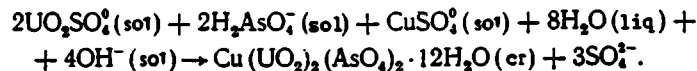
We will now examine the conditions of thermodynamic equilibrium of minerals of a similar cation composition of two related groups of uranium micas — uranyl arsenates and uranyl phosphates; for the comparison we will examine the Cu-containing pair: zeunerite-torbernite (Fig. 3). Calculations indicate that in the acid and neutral regions the former mineral should be formed when the concentration of arsenic acid (and its dissociates) in the solution is double that of the phosphoric acid; in the region of higher pH values (8-11), its concentration should be three times as high. According to aggregate data of Shvartsev [11], the mean content of P in groundwater of the hypergenesis sphere is 57.5 $\mu\text{g/liter}$; that of As just 2.07 $\mu\text{g/liter}$; thus, a concentration of the second element higher by two or three times than that of the first can only be achieved with an additional source of arsenic — namely, this component in an arsenide, sulfarsenide, authigenic or ionic forms must be present in the uranium ore accumulations being oxidized. The concentrations of arsenic acid dissociates in oxygenated groundwater in such instances can be as high as tens and even hundreds of milligrams per liter [9], i.e., sufficient for the formation of uranyl arsenates but not other uranium micas. The conclusion by Belova [1] and Chernikov [9] to the effect that uranyl arsenates are specific minerals of the oxidation zones of endogeneous uranium deposits whose primary ores are relatively rich in arsenic (as different from uranyl phosphates, which are minerals of the oxidation zone of sulfide-uranium and not phosphorus-uranium deposits [3]) is therefore fully justified.

The formation of uranyl arsenates can probably occur in two ways:

1) directly during the oxidation of primary minerals by oxygenated uranium-bearing groundwaters of any acidity, such as in the oxidation of arsenopyrite:



2) during the neutralization of solutions abruptly acidulated in the course of oxidation of As-containing sulfide-uranium ores according to the reaction



This latter mechanism seems to be more widespread, as it gives rise to a broad spectrum of arsenic-uranium micas; their variety reflects not only the variations in the source of specific cations [9], but largely also the tendencies in the change of the alkaline-acid indicator of the medium and the overall mineral salt content of the water. As the maximum acidity front, corresponding to the peak of sulfide oxidation and sulfuric acid generation, advances (the second stage of uranium ore oxidation according to Belova [1]), the Ca- and Mg-uranyl arsenates formed previously would be replaced by zeunerite; as these minerals are displaced toward the rear portion of the profile of oxidative zonality, they can again be replaced by calcium-, magnesium-, or (in the subsurface settings of arid provinces) sodium-uranospinite.

The third hypothetical mechanism of formation of uranyl arsenates during neutralization of alkaline solutions in natural conditions is unlikely, as groundwaters enriched in As in the oxidation of endogenous As-containing uranium ores can rarely be alkaline; the ordinary "background" waters, however, are incapable of providing As in amounts sufficient for the synthesis of these minerals because of the low clark of this element in the earth's crust ($1.7 \cdot 10^{-4}\%$ according to Vinogradov [5]) and permeable sedimentary strata ($1 \cdot 10^{-4}\%$ in sandstones according to Tarkian and Wedepol [5]).

The close association of uranyl arsenate accumulations with uranium ore endogeneous As-containing source thus practically rules out the possibility of a genuine infiltrational development of these uranium micas. This distinguishes them from uranyl phosphates and uranyl vanadates; the latter groups of minerals occur as exogenous-epigenetic ore accumulations, representing primary uranium mineralization in deposits of carbonaceous schists and calcretes [3, 4, 12]. This fact should be taken into account in genetic interpretations and the sorting out of subsurface uranium accumulations in arid provinces.

* * *

1. Experimental studies have produced the values of the products of solubilities of four synthesized uranyl arsenates corresponding to natural minerals: hydrogen uranospinite ($10^{-45.58 \pm 0.06}$), calcium uranospinite ($10^{-45.76 \pm 0.05}$), novacekite ($10^{-44.44 \pm 0.11}$), and zeunerite ($10^{-44.96 \pm 0.13}$). The calculated values of $\Delta G^\circ f_{(298.15)}$ of the minerals (disregarding crystallization water) are: $(\text{H}_2\text{O})_2(\text{UO}_2)_2(\text{AsO}_4)_2 - 843.35 (\pm 0.08)$; $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 - 961.34 (\pm 0.07)$; $\text{Mg}(\text{UO}_2)_2 \cdot (\text{AsO}_4)_2 - 936.23 (\pm 0.15)$; $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 - 819.35 (\pm 0.19)$ kcal/mol.

2. With the newly calculated thermodynamic constants and the previously published data of Chukhlantsev and Sharova on sodium uranospinite and abernatite, it has been established that the solubility of uranyl arsenates depends largely on the pH of the medium: it rises rises largely in ultraacid and alkaline regions and is minimal in low-acidity-near-neutral regions (pH 5-7). H-uranospinite is formed in a highly acid environment and gives way progressively during neutralization of solutions to zeunerite and, further, in neutral and alkaline settings to calcium uranospinite. An additional magnesium source in the rocks being oxidized is necessary for novacekite formation. Zeunerite can be considered, in addition, to be a characteristic mineral of the oxidation zone of arsenic-uranium ores in humid provinces, and Ca-uranospinite in arid provinces. Na-uranospinite is formed only provided a very high activeness of sodium, which is typical for highly mineralized groundwaters of Recent extra-arid regions. It can be replaced by abernatite only at abnormally high potassium concentrations in the solution, which is probably attainable in settings of intensive decay of the corresponding aluminosilicates in the course of oxidative weathering of ore-bearing rocks.

3. Unlike uranyl phosphate mineralization, uranyl arsenate mineralization requires high concentrations in the mineral-forming solutions of the appropriate anionogenic component — arsenic; i.e., it must be present in the uranium ores being oxidized. The principal mechanism of the formation of such secondary accumulations of uranyl arsenates is neutralization of groundwaters abruptly acidulated by oxidation of endogenous sulfide-uranium rocks rich in As. This mineralization can also appear as a result of direct interaction of uranium-oxygenated groundwater of any acidity with rocks containing As minerals. The development of true infiltration ore accumulations of uranyl arsenates is highly unlikely, which is an observation important for determining the genetic types of sorting out the subsurface shows of uranium in arid provinces.

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VARIEGATED BATHONIAN ROCKS OF THE SOUTH FERGANA VALLEY
(DATA ON AGE AND GENESIS)

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UDC 552.51:552.52:551.762(575.13)

Alluvial and proluvial sediments have been identified on the basis of a detailed lithologic and facies analysis of the top of the Middle Jurassic in Sulyukta coal deposit. The Bathonian age of red proluvial clays with plant imprints has been confirmed. A sedimentogenic origin of the red pigmentation of the proluvial Bathonian rocks has been determined; these rocks were formed in a setting of progressively more arid climate.

Jurassic sediments are widespread in the Fergana depression. They are exposed along the sides of the depression and sink deeper toward its inner portions, where these sediments are identified by bore holes. The Bathonian rocks are of an exclusively continental genesis and exhibit a facies variability both in section and in plan; the thicknesses vary at relatively small distances. Paleontologically, the rocks are poorly characterized, and there are no reliable marking horizons. This makes it difficult to separate, date, and correlate these entities. The age of the locally named suites is estimated mainly from rare plant remains and freshwater bivalve mollusks.

Pay coal deposits in the southern Fergana depression have been studied in more detail. The Jurassic of South Fergana has been described in [2, 9, 16, 20], where stratigraphy and lithology were studied.

In 1935 a stratigraphic classification of the South Fergana Jurassic was undertaken for the first time by M. I. Brik based on floral remains. She divided the Jurassic into two horizons — the Lower and Upper Liassic — traced through coal beds of Kyzylkiisk and Sulyukta coal deposits. There are not data on the Middle Jurassic of South Fergana.

A more detailed Jurassic classification for the area of Sulyukta brown coal deposit was suggested by Preobrazhenskii [16]. His scheme was based on distinct rhythmic patterns in the strata; he identified rhythms (suites) consisting mainly of sandstone, clay, and coal separated by conglomerate members and traceable throughout the deposit. The rhythms were identified by letter indices A, B, C, ..., H₁-H₈.

In the "Resolutions of the Conference on Unified Stratigraphic Schemes for Soviet Central Asia" [17], Sulyukta Jurassic sediments were combined into a Sulyukta suite; its upper boundary (the boundary of the Precretaceous washout) lay not higher than the Bathian stage.

In 1971 the Interagency Stratigraphic Conference on the Mesozoic of Soviet Central Asia renamed the Sulyukta suite the Samarkandek suite; the upper boundary of this newly named suite was lowered on the recommendation of Genkina et al. [10] to the boundary between the Bajocian and Bathonian.

Stratigraphic studies in Sulyukta were parallel to investigations of the lithology of the Jurassic; most attention, naturally, was paid to coal-bearing beds. Within the Sulyukta deposit the Jurassic coal-bearing sediments underlying variegated rocks are up to 400 m thick; they appear as a bed of rhythmically interstratified conglomerates, sandstones, and clays with coal.

Numerous investigators [5, 9, 21] indicated earlier that toward the end of the Middle Jurassic the climate in Central Asia and, in particular, in the Fergana Valley, became more arid; previously, during the Early and Middle Jurassic, it was humid. Due to aridization the palustrine facies widespread in the Liassic-Dogger disappeared from the set of facies, while proluvial facies appeared; up the profile, the proportion of red pigmentation increased against the overall gray-green color; down the profile, coalified attritus became reduced, the role of

Geological Institute, USSR Academy of Sciences, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 55-61, May-June, 1987. Original article submitted July 14, 1986.

TABLE 1. Genetic Types and Facies of the Middle Jurassic of South Fergana (Sulyukta)

Genetic type	Indexes		Facies
Alluvial sediments			
Coarse and small pebble conglomerates, small-grained gritstone; rounding; 3-4 points (75-100%); sorting: relatively good, sometimes slightly rhythmic; stratification: coarse, oblique, unidirectional, slightly pronounced; color: gray, often with rusty spots and stripes.	ARG-1	ARG	Gravel-pebble sediments of mountain riverbeds.
Medium- and coarse-grained sandstone, sometimes with gravel; sorting: good, indistinct, rhythmic; stratification: coarse, oblique, less often fine unidirectional, converging; color: gray, gray-green with rusty spots and stripes.	ARD-1		Sandy sediments of small plainland rivers.
Medium- and small-grained sandstone; sorting: good, slight rhythmic; stratification: small, less often coarse, oblique, unidirectional, converging; color: gray-green with rusty spots and stripes.	ARPG-2	ARP	Clay-silt sediments of floodlands.
Small-grained sandstone and siltstone; sorting: good, often unclear rhythmic; stratification: small, horizontally waved lenslike to horizontal; color: from gray with brown spots and smears to dark brown.	APG-1		
Coarse- and small-grained siltstone clay, often in fine interstratification; good sorting; small horizontal, less often horizontal-wavy interrupted stratification, frequently underlain by coalified attritus; color: gray-green with brown spots.	APG-2	APG	
Proluvial sediments			
Small-pebble conglomerates, gritstones, sandstones; pebble rounding: 0-2 points (0-50%); sorting: locally from poor to good; stratification: coarse and small, oblique gentle, indistinct; color: brown, pink, to gray spotty.	PK-1	PK	Gravel-pebble sediments of alluvial cone streams
Coarse- and small-grained sandstone, sometimes with gravel; poor sorting; small oblique, gentle, indistinct stratification; color: brown to yellow, pink, spotty.	PSL-1		Sand-clay sediments of the tails of alluvial fans.
Coarse- and small-grained siltstone clays with poor sorting; stratification: small, horizontal, and horizontal-wavy, indistinct, less often oblique wavy and line-wavy, locally lenslike; color: yellow, pink, red.	PSL-2	PSL	

kaolinite among clay minerals diminished, while smectites and mica-smectites appeared [6]. Toward the end of the Dogger the floral pattern changed, acquiring xerophytic features and losing moisture-loving plants [11].

Until recently, little attention was given to genetic interpretations of the Jurassic in the Fergana depression; stratigraphic positions of variegated and red rocks at the top of the Sulyukta profile had never been discussed; the author attempted to determine the age and genesis of the upper variegated portion of the Jurassic of this section (rhythms H_3 - H_4). The present study is an element of a general exploration of the lithology of the Middle and Upper

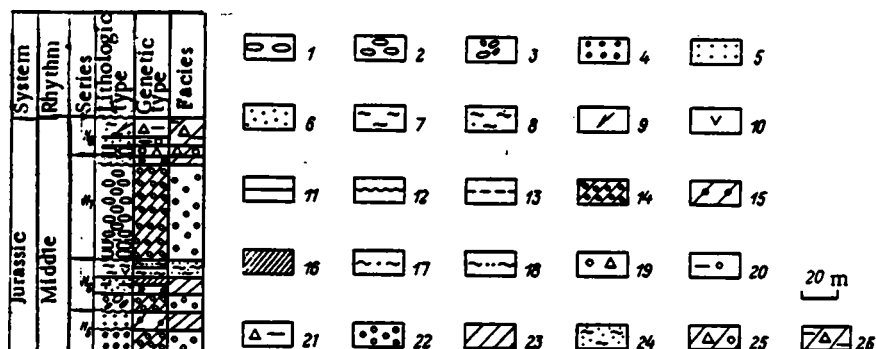


Fig. 1. Schematic lithologic-facies profile of the Middle Jurassic of Sulyukta (top portion): Lithologic rock types, inclusions, and contacts: (1-3) conglomerates (1 - coarse pebble; 2 - medium pebble; 3 - small pebble); (4) coarse- and small-grained gritstone; (5, 6) sandstone (5 - coarse-grained; 6 - medium- and small-grained); (7) clay; (8) sandy clay; (9) plant imprints; (10) coalified attritus; (11) distinct contact; (12) washout; (13) gradual transition. Genetic type. Alluvial sediments: (14) ARG-1; (15) ARP-1; (16) ARP-2; (17) APG-1; (18) APG-2. Proluvial sediments: (19) PK-1; (20) PSh-1; (21) PSh-2. Facies. Alluvial: (22) gravel-pebble sediments of mountain riverbeds (ARG); (23) sandy sediments of small (plainland) riverbeds (ARP); (24) clay-silt floodland sediments (APG). Proluvial: (25) gravel-pebble sediments of alluvial fan streams (PK); (26) sand-clay sediments of alluvial fan tails (PSh). See Table 1 for expansion of abbreviated indexes.

Jurassic variegated rocks in the Fergana area [6]. The Sulyukta profile was chosen, because the changes of the lithology and facies of the sediments caused by the drying of the climate at the end of the Late Jurassic were better defined here; it was also possible to establish unequivocally the Bathonian age of the variegated and red rocks in this area.

Our study was mainly based on a detailed lithologic and facies investigation [22, 23]; we have identified in the profile of the Sulyukta area several genetic sedimentary types combined into the following facies: gravel-pebble sediments of mountain riverbeds (ARG); sandy sediments of smaller plainland riverbeds (ARP); clay-silt sediments of bayous (APG); gravel-pebble sediments of alluvial cones (PK); and sand-clay sediments of alluvial cone tails (PSh).

The characteristics of the genetic sedimentary types of the various facies are given in Table 1.

A regular alternation of the genetic sedimentary types and their facies in the profiles forms alluvial rhythms. At the base of the first Bathonian rhythm (H_1) are coarse-gravel mountain riverbed sediments relatively well sorted and rounded, with a slight large oblique uniform stratification (ARG facies). Up the section, one sees on an uneven boundary sediments formed in the environment of a small plainland river; these are coarse-grained well-sorted sandstones with large and small oblique uniformly directed converging stratification (ARP facies). The upper floodland portion of the rhythm seems to be eroded, because it is overlain with a washout by the base deposits of the next cycle (H_2), consisting of small pebble conglomerates of a mountain riverbed with an indistinct coarse oblique evenly directed stratification. These strata are overlain by plainland riverbed sand sediments, consisting of two genetic types (ARP-1 and ARP-2), gradually succeeding one another. The rhythm is completed by gray-green floodland sediments consisting of well-sorted siltstone and clay with small horizontal stratification underlain by coalified attritus (genetic types APG-1 and APG-2). At the base of the next rhythm (H_3) a thick member of coarse pebble and further middle-pebble conglomerates occurs with a washout; these sediments were formed in a mountain river valley (ARG facies); up the section, they are succeeded abruptly by thin alluvial small-sand sediments (ARP facies).

The next rhythm up the section (H_4) is an entirely different genetic entity. At its base, ill-sorted sediments with an erosion surface; these are slightly aggregated small-pebble conglomerates with gravel-sand-clay cement, which include some practically unrounded rock fragments and exhibit indistinct oblique low-angle stratification (the alluvial cone stream facies PK). They are overlain with an indistinct boundary by pink inequigranular gravelly sandstone, with indistinct small oblique stratification (PSh-1). The rhythm is crowned by

silt-clay rocks with small horizontal and horizontal-wavy indistinct stratification which were formed in the zone of the proluvial tail (PSH-2) (see Fig. 1).

It was earlier determined [3, 20, etc.] that the Jurassic of Sulyukta accumulated mainly in a sublatitudinal river valley. Our study showed that the sediments in this part of the profile (rhythms H_5 - H_8 , as described by Preobrazhenskii) have also been formed in a mountain-river valley flowing from west to east. The presence of better-rounded and sorted conglomerates of mountain riverbed facies (ARG) separated by thick floodland and bayou clay members (APP, ATsG) confirms the existence of a facies setting of this kind (see Table 1 and Fig. 1). Some of the lithologic and facies traits of this part of the profile are indicative of a climatic aridization that set in at the end of the Middle Jurassic. It is seen in a poorer sorting of clastics and in the rounding due to the progressively stronger activity of seasonal water streams typical for arid areas. Compared with the humid climates, water streams in such territories sooner grow shallow after flood tides, lose much of their energy, and discharge less-well-sorted material. At the same time, local areas, probably close to the banks of the principal valley and smaller side tributaries, develop facies conditions similar to proluvial settings. Shantser [25, 26] has demonstrated that there are no distinct boundaries separating the true proluvial sedimentation environments from alluvial settings. These genetic groups of sediments are connected by numerous transitional forms, occupying an in-between position in the classification. Field studies of stratification, sorting, and rounding of clastic material and other primary genetic features combined with granulometric investigations allowed us to identify within the rhythm H_8 a proluvial facies complex in addition to the alluvial complex (Fig. 1). The red color is an indirect confirmation of a proluvial genesis of this sedimentary portion. Coalified attritus, abounding in the gray-green underlying bed is practically absent here; the sediments contain numerous plant imprints, with a completely oxidized organic part. The areas of local lighter pigmentation around the imprints indicate a process of diagenetic gleying of the red rocks [15].

These imprints were collected by us for the first time during the field season of 1984 from the very top of the Jurassic, 5 m beneath the Cretaceous contact in crimson red clay.

Duludenko, who made the floral determinations of the imprints, notes that plant remains were poorly preserved; in most imprints the veins are not preserved, making it difficult to identify the species or even the genus (*Nilssonia* or *Taeniopteris*) the set of plants consists of horsetail *Equisetites beani* (Bund.) sew and roots of *Radicitis* sp., classified as horse-tails; ferns of the species *Sphenopteris-Coniopteris* (no fertile fronds have been found, so they cannot be strictly identified as *Coniopteris*) similar to *Coniopteris embensis* Pryn., *C. spectabilis* Pryn. Cycadic species are represented by entire-edge leaves *Nilssonia-N. ex gr. orientalis* Heer, *N. vittaeformis* Pryn., *N. Polymorpha* Schenk. A small fragment of a segmented leaf can be referred either to *Nilssonia* (very poor preservation) or *Pterophyllum* (very poor preservation). The predominance of horsetails, ferns, and cycadophytes (p. *Nilssonia*) indicates the Middle Jurassic age of the flora. The presence of small-frond species (*Sphenopteris-Coniopteris*) indicates the upper half of the Middle Jurassic or Bathonian age of this flora. This conclusion, drawn by Duludenko, is not at variance with the classification [18] placing the upper boundary of the Jurassic in Sulyukta (the Pre-Cretaceous erosion boundary) not above the Bathonian. Our data thus clearly confirm the Bathonian age of red sediments.

For comparisons of the Jurassic of South Fergana, plant remains from variegated sediments of the Shurab deposit are of interest. At the top of the Igrysai suite, previously referred to the Upper Jurassic as an element of the previous Shurab suite, a collection of plant imprints has been described by Duludenko as Bathonian. The list of flora defined from imprints includes the ferns *Coniopteris-C. angustiloba* Brick., *C. fursenkoi* Pryn., *C. spectabilis* Brick.; ginkgo, a single imprint of *Sphenobaiera* fragment, two imprints of different *Ginkgo* species which can be defined as *Ginkgo* sp. 1 and *Ginkgo* sp. 2; czekanowski species, *Czekanowskia rigida* Heer.; coniferous, numerous *Ferganiella lanceolata* Brick., rare *Podozamites eichwaldii* Heer and *Pitiophyllum angustifolium* (Nath.) Moeller, *Pitiocladus* sp.; and cycadophytes *Anomozamites quadratus* Prosvir.

In conjunction with the stratigraphic position of this bed and its lithology and facies, the genesis of the red pigmentation of flora-bearing sediments raises an important question: is it primary (sedimentogenic) or secondary (postsedimentary)? This problem has been discussed in numerous publications [1, 4, 12, 13, 24, and others]. We believe that the red coloring of the rocks in this region developed as follows.

During the Pre-Jurassic and Jurassic (?) red crust formation evolved intensely on the territory of the ancient Fergana depression and adjacent regions with hot tropic climate [8, 14, 19]. Rewashing and redeposition products of these crusts must have played an important role in shaping the sedimentary cover of the Fergana depression during the Jurassic. This is evidenced by the composition of sandstones, where quartz and silicic schist fragments account for 80-90% (apogranitic graywacke complex [27]) and the predominantly kaolinitic composition of clay minerals with a subordinate content of hydromica, chlorite, and an admixture of smectite content of hydromica, chlorite, and an admixture of smectite and mica-smectite [7]. The gray and gray-green color of the sediments of most of the Jurassic were formed with contribution of abundant organic material that converted ferrous iron to ferric forms. The red material redeposited from crusts of weathering thus lost its pigmentation in the sedimentation basin. The aridization that set in at the end of the Middle Jurassic, combined with weakened tectonics and the paleogeographic situation that took shape, drastically reduced the amounts of buried organic material, which was no longer sufficient to produce widespread reductive settings. The iron brought from crusts of weathering thus could be fixed in an oxide form and color rocks red.

The red color also indirectly confirms a proluvial genesis of sediments accumulated in sharply variable dynamics of the water environment of seasonal streams with an intense and uneven oxidation of iron and organic matter. The authors have analyzed the distribution of iron forms in clay sediments of a proluvial tail; specimens were collected from adjacent interlayers of a blue-gray and red color. Three types were studied: 1) the originally gray stratum, which acquired a secondary superimposed pigmentation during postsedimentary processes; 2) the originally red layer, which became variegated with interlayers of differently colored rocks; and 3) the originally variegated layer that retained its diverse pigmentation during the postsedimentary history.

In the first and second cases, where the color was superimposed by secondary epigenetic (hydrogenetic) processes (iron brought in by iron-humate solutions, oxidation of scattered siderite, etc.), the original contents of the different iron forms should obviously be approximately equal, which is the reason for a uniform (either gray or red) pigmentation. The superposition of secondary processes ought to have disrupted the primary homogeneity in the distribution of iron forms and either reduce the content of ferrous iron by increasing the proportion of ferric iron and forming a red pigmentation, or increase the content of ferrous iron by reducing the ferric form and removing the red color.

Analysis shows that the transition from a blue-gray color to a distinct red is associated with a nearly doubling of both ferrous (from 0.84 to 1.54%) and ferric (from 1.17 to 1.92%) iron. There are thus grounds to believe that variegation here is primary and that the pigmentation formed during the sedimentogenesis and diagenesis was not altered by secondary processes.

* * *

The following conclusions are drawn from the study:

1. The set of genetic types and facies identified in the sections indicates that the rocks in this part of the profile were formed mainly within a valley of a mountain-plainland river, except for the rhythm H₂, locally associated with proluvial sedimentation settings.
2. The set of plant imprints from red clays of the rhythm H₂ in Sulyukta profile and comparisons with the similar set of Igrysa suite of Shurab indicate that this part of the profile is of a Bathonian age.
3. The red color of the clays of the rhythm H₂ was produced by climatic aridization at the end of the Middle Jurassic and is sedimentogenic.

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On the basis of most recent lithostratigraphic data a generalized Late Precambrian siliceous-carbonate phosphorite formation with which is associated major phosphate deposits of the eastern part of the Kuznetsk Alatau was separated into a number of independent formations: siliceous-dolomite (R_s), dolomite (R_s-V), siliceous-carbonate in a narrow sense (R_s-V), and siliceous-shale-carbonate (V). Data on phosphate deposits of the volcanogenic-siliceous-carbonate formation ($V-c_1$) are presented. The newly separated formations are shown to differ not only in composition and structure but also in paleotectonic zoning, distribution of useful minerals, and in local ore control factors. The prospects of discovering new phosphorite deposits in the area of study are examined.

The phosphorites known in ancient, predominantly Late Precambrian formations of the eastern half of the Kuznetsk Alatau are micrograined or aphanitic sedimentary rocks. They were discovered in the early 60s [7] at which time the first ideas of their genesis were formulated, local distribution patterns of phosphate ores were determined, and potential sites of mineral deposits were preliminarily explored. From these facts it was inferred that the great bulk of the phosphorites was confined to the thick, predominantly carbonate formation of Upper Riphean age. This formation was named the carbonate-siliceous or siliceous-carbonate phosphorite formation [7, 10]. Somewhat later, in the east of the Kuznetsk Alatau, another younger phosphorite formation — Early Cambrian volcanogenic-siliceous-carbonate — was distinguished [8]. A description of these two formations was subsequently refined and expanded in detail; the lithostratigraphic basis for their classification remained unchanged.

New recently published data on phosphorite deposits, stratigraphy, lithofacies analysis, and paleotectonic zoning [4, 6] call for a careful review of earlier ideas on the volume, character, and relations of phosphorite-bearing rock associations of the eastern part of the Kuznetsk Alatau. Instead of a single siliceous-carbonate formation, which, as it turned out, is a composite formation, the main thrust of the proposed changes was on separating the following already observed Late Riphean-Vendian lithocomplexes (formations) in a section of the Precambrian: siliceous-dolomite, dolomite, siliceous-shale-carbonate, and siliceous-carbonate (Fig. 1). In addition, the volume and characteristics of the Lower Cambrian volcanogenic-siliceous-carbonate formation were more specifically defined. Suites as local lithostratigraphic subdivisions were used to identify the formations. Areas composed of Upper Riphean and Vendian formations undifferentiated into suites are shown in Fig. 1 as an undivided carbonate formation.

We shall examine the above formations as they apply to an earlier developed [4] scheme of geotectonic zoning of the eastern part of the Kuznetsk Alatau, by which the following areas from north to south were distinguished: the Beloiys-Bellykskii trough, the Batenevskaya intermediate zone, the Azyrtal uplift, and the Saksyrskaya zone (see Fig. 1).

The Siliceous-Dolomite Phosphorite Formation R_s was distinguished in a volume of the Charyshtag and coeval Ulugzas suites [6]. It covers large areas in the east of the Azyrtal uplift (Azyrtal mountain range) and is also extensive in some areas of the western part (the Tom' and Askiz interfluvium). The principal constituent of the formation is dolomite; limestones and transitional limestone-dolomite varieties are present in small amounts; cherts are an obligatory constituent of the formation. The thickness of the formation reaches 3000 m, 70% of which is dolomite. In type sections the siliceous-dolomite lithocomplex is a fairly uniform alternation of variably silica-saturated dolomites and limestones, which is disrupted

Siberian Scientific-Research Institute of Geology, Geophysics, and Mineral Raw Materials, Novosibirsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 62-70, May-June, 1987. Original article submitted June 6, 1985.

TABLE 1. A Summary Table of Phosphorite Formations of the Eastern Part of the Kuznetsk Alatau

Formation	Thickness, m	Suite	Paleotectonic Zoning	Character of Phosphate Distribution	Predominant Phosphorite Type	Ore Control Factors
Siliceous-dolomite (R ₃)	Up to 3000	Charyshtag, Ulugzas	Uplift	Ubiquitous, low phosphate content	Detrital, organogenic	Reef-associated facies of the uplift margin
Dolomite (R ₃ -V)	Up to 1200	Khabzas, Martyukhina	Uplift	Episodic	Pelitomorphic	Most mobile areas of the paleobasin
Siliceous-carbonate (R ₃ -V)	Up to 1500	Litvinskaya	Transition zone from uplift to trough	Sharply discon- tinuous "pocket- shaped"	Pelitomorphic	Not det'd.
Siliceous-shale- carbonate (V)	Up to 600	Sorninskaya	Uplift	Ubiquitous, uneven	Pelitomorphic	Not det'd.
Volcanogenic-silice- ous-carbonate (V-C ₁)	Up to 1800	Tamalyk	Margin of Early Cambrian super- imposed trough	Presence of large phosphorite de- posits, rapid wedge-out of phos- phorite horizons	Pelitomorphic	Presence of volcano- genic rocks in the section, absence of rhythmic succession

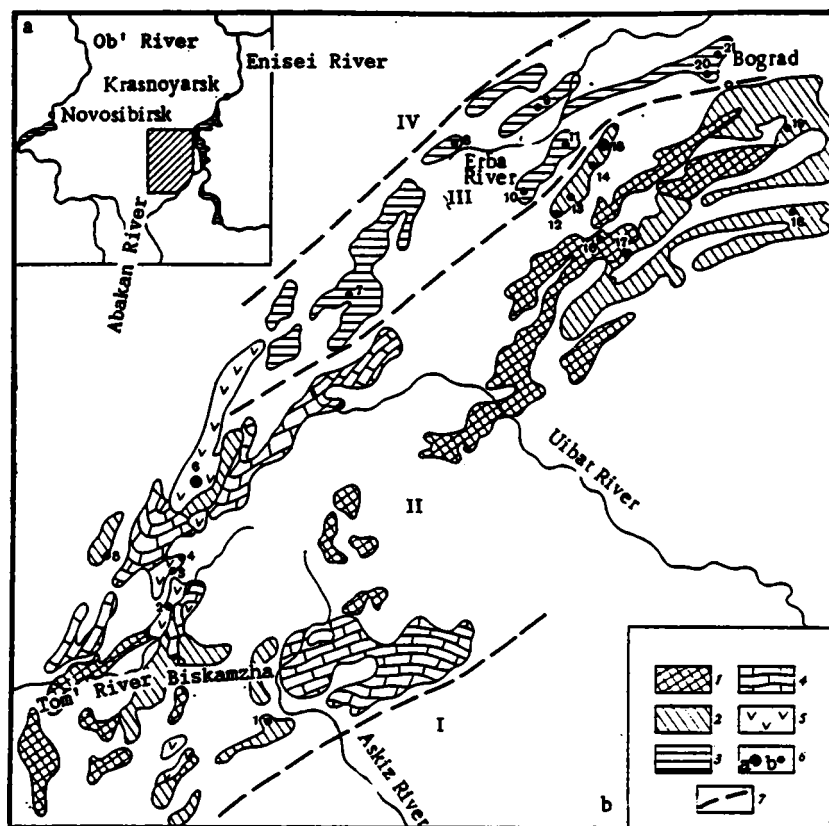


Fig. 1. Location (a) and distribution of phosphorite formations of the eastern part of the Kuznetsk Alatau (b). 1-5) phosphorite formations (1 - siliceous-dolomite R₃, 2 - dolomite R₃-V, 3 - siliceous-carbonate R₃-V, 4 - undivided carbonate R₃ + V, 5 - volcanogenic-siliceous-carbonate V-Є₁); 6) deposits (a) and occurrences (b) of phosphorites; 7) boundaries of geotectonic zones and subzones. Phosphorite occurrences: 1) Khabzas; 2) Tomsk; 3) Karatasnsk; 4) Kanava 156; 5) Kanizassk; 6) Tamalyk (deposit); 7) Vershinka; 8) Sonskii; 9) Yulinsk; 10) Tyrdanovsk; 11) Karasynsk; 12) Sukhoe Lake; 13) Osinovsk; 14) Davidkovsk; 15) Obladzhansk (deposit); 16) Tinsk; 17) Kuten'buluusk; 18) Sonontsovsk; 19) Voroshilovsk; 20) Kanava 280; 21) Bograd. I) Margin of the Azyrtal uplift (Saksyraskaya zone); II) Azyrtal uplift; III) Batenevskaya zone; IV) Beloiyus-Bellyskii trough.

by the occurrence of thick homogeneous dolomite members. The highest concentrations of cherts are in the lower and upper parts of the formation. Cherts (generally dark-colored), which occur in the form of horizons, beds, and interlayers among carbonates, are sedimentation units, while cherts, which form pockets, lenses, and reticulate-streaky and spotted inclusions, are considered by us to be epigenetic. The great bulk of the rocks is dark-colored with fine-grained textures, which bear testimony to their chemogenic origin. The organogenic varieties are present in small amounts over most of the area of the formation. They are represented by light-colored stromatolitic dolomites and typical oncolitic siliceous-carbonate formations composed of members several hundred meters thick.

Widely occurring phosphate deposits are typical of the complex under consideration. Weakly phosphatized rocks (0.2-0.3% P₂O₅) occur throughout the section. The highest (2-3%) concentrations of phosphorus pentoxide are in cherty beds and lenses of siliceous-carbonate members in the upper and lower parts of the formation. The thickness of the phosphatized horizons, based on point sampling data, reaches 100 m.

Across the strike of the Azyrtal uplift the siliceous-dolomite formation shows definite changes. In the vicinity of the north margin of this paleostructure the chert content decreases sharply, and limestones disappear from the section. The formation appears to be largely represented by organogenic dolomites, including horizons of dolomitic breccias and beds of oncolitic siliceous dolomites. Associated with these formations are phosphorites of the Tinsk occurrence. The productive member of the occurrence, 30-40 m thick, is composed

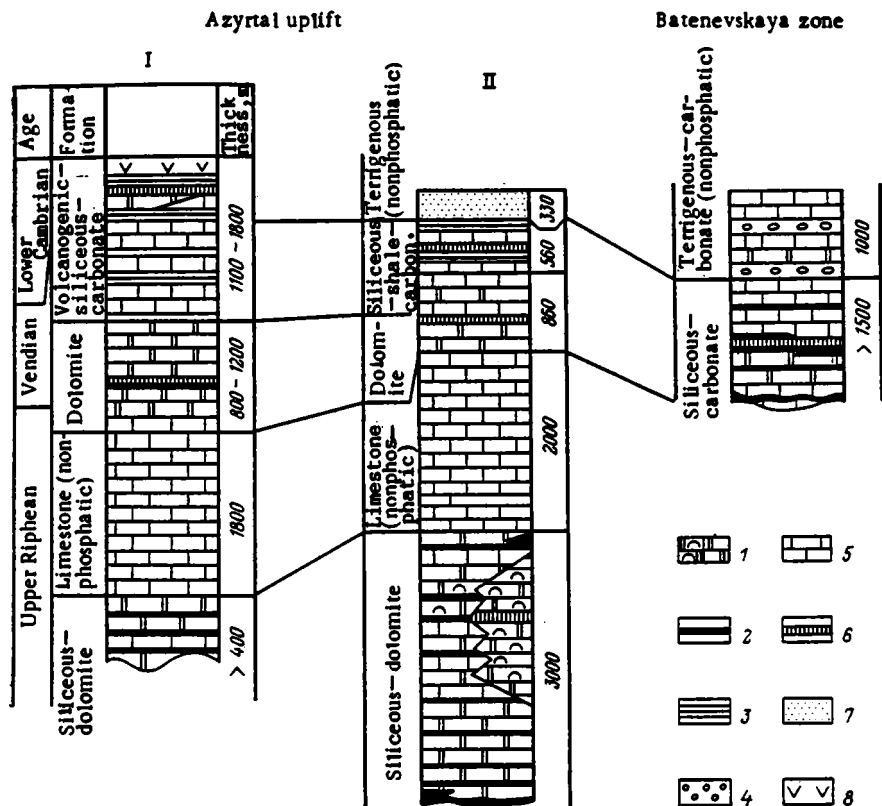


Fig. 2. Comparison of the phosphorite formations of the eastern part of the Kuznetsk Alatau. 1) dolomites (a - stromatolitic, b - other); 2) limestones; 3) cherts; 4) phosphorite horizons; 5) siliceous, clay-siliceous, siliceous-calcareous shales; 6) sandstones; 7) conglomerates, gritstones; 8) basic extrusive rocks; I) Tom' and Khabzas interfluvium; II) Azyrtal mountain range.

of phosphorite layers interbedded with phosphatic dolomites. The P_2O_5 content varies widely (on conversion to a member thickness of 4.6%). Microscopically the phosphorites are a detrital rock consisting of angular phosphate fragments (isotropic or weakly crystallized, with a preserved oolitic texture in place) and micrograined dolomites. The fragments are enveloped by concentric beds of dolomites, forming an organogenic-like texture.

The occurrence of organogenic facies near the north margin of the Azyrtal uplift may be due to the shallow waters of this part of the basin induced by the proximity of the Batenevskaya mobile zone, which outcropped as a relative uplift. These conditions, which lasted a long time, proved to be favorable for the formation of phosphorite layers. Over the remaining area of the siliceous-dolomite formation sedimentation occurred in a deeper water environment.

The Dolomite Phosphorite Formation (R_3-V) was distinguished in the Azyrtal mountain range in a volume of the Martyukina suite and in the Askiz and Tom' interfluvium in a volume of the Khabzas suite [6]. The principal constituent of the formation is dolomite. Limestones and dolomitic limestones, which make up 20% and, in some cases, 50% of the volume of the formations, are present in varying amounts. In addition, cherts and siliceous-clay shales occur as accessory constituents. In vertical succession the dolomite formation is underlain by a non-phosphatic limestone formation and overlain by siliceous-shale-carbonate or volcanogenic-siliceous-carbonate phosphorite formations (Fig. 2). It differs from the siliceous-dolomite formation in that the character of alternation of the major formation-producing constituents - dolomite and limestone - is different and the role of cherts is minor (to the extent of being nonexistent). In a lateral direction the dolomite formation to some degree (in places, considerably) changes its composition and structure. For example, in the southwest of the Azyrtal uplift, it consists mainly of light-colored dolomites, which include, in isolated cases, limestone members and horizons of cherts and siliceous-clay shales. In the northeastern part of this paleostructure the role of limestones increases in the volume of the formation. Here its section often represents an alternation of large limestones and dolomite members;

mutual contacts along the strike of individual horizons and beds of dolomite and limestone are typical. The great bulk of the carbonate rocks (mainly dolomite) shows signs here of an organogenic origin. The thickness of the formation is on average 1000-1200 m.

A somewhat elevated phosphate content is observed in many areas of the dolomite formation. Well known are several occurrences of phosphorites confined to dolomites and limestone dolomites in the northern part of the Azyrtal uplift (Osinovsk, Sukhoe Lake, etc.). The phosphorites form 0.1-0.5-m-thick lenses containing 11% P_2O_5 , which are enclosed among weakly phosphatic rocks. The thickness of the phosphorite horizons is 50 m. Phosphatic rocks which contain 1-3% P_2O_5 are quite extensive in area. The Obladzhansk deposit of secondary phosphorites was formed from the Mesozoic-Cenozoic weathering of phosphatic rocks of the dolomite formation. In the southwestern part of the uplift the Khabzas phosphorite occurrence (Askiz River basin) is well known. The section of the dolomite formation in this area is represented by dolomites, which include members of limestones, siliceous and clay shales, and cherty beds. The phosphorite horizon is confined to the middle of the section and is composed of dark-gray and gray laminated dolomites with beds and lenses of black cherts and dolomite siliceous breccias. The phosphorites have a laminar and brecciated structure; they form 0.3-m-thick lenses and beds, which differ little macroscopically from the enclosing rocks. In the non-phosphatic part they are siliceous-dolomite with a P_2O_5 content in lump samples ranging from 4 to 22%. The texture of the phosphatic material itself is pelitomorphic.

The composition of the dolomite formation should generally be considered favorable with respect to phosphorite content, since, as we know, most of the large deposits of Precambrian and Cambrian phosphorites are associated with dolomite formations. A possible cause of the weak productivity of this lithocomplex is the high stability of the Azyrtal uplift in Martuykhina time and the uniform sedimentation conditions within it. This is borne out by the fact that the phosphorite occurrences in the formation are known only within the most mobile areas of the paleobasin. They include the northern extremity of the Azyrtal uplift adjacent to the Batenevskaya zone and the southwestern part of this paleostructure, which comprises the east margin of the newly formed Balyksa through developed apparently at the end of the Late Riphean-Vendian [4]. Confined to the latter area is the above-mentioned Khabzas occurrence, whose section differs from other sections of the dolomite formation in having a highly contrasting structure suggestive of the pulsation of tectonic movements.

The Siliceous-Shale-Carbonate Phosphorite Formation (V) was distinguished in a volume of the Sorninskaya suite and was separated only in the Azyrtal mountain range (Fig. 1 shows the areas of its occurrence together with the dolomite formation). Compared to the rock complexes above, its composition is more variegated. The principal constituent of the formation is limestone, generally dark-colored, massive, and bedded. Siliceous, clay and siliceous-clay shales make up at least 30% of the volume of the formation. Dolomites, cherts, and siliceous siltstones occur in very small amounts. In general, the section of the formation is an alternation of 100-m thick members of limestone with complex carbonate-clay-siliceous horizons a few tens of meters thick. The thickness of the formation reaches 660 m.

In a lateral direction, southwest of the Azyrtal uplift, this association passes into a volcanogenic-siliceous-carbonate phosphorite formation, which is the stratigraphic equivalent of its lower part [6].

The phosphate content of the siliceous-shale-carbonate formation manifests itself on some scale nearly everywhere within the area of its occurrence. It is confined to an essentially carbonate-clay-siliceous horizon, which lies in the middle of the section. Associated with this horizon is a number of phosphorite occurrences and mineralizations. The phosphorites are generally black, pelitomorphic, and siliceous with a phosphate content of 10% P_2O_5 . The phosphorite beds reach a thickness of 0.2 m, sometimes more. The formation is characterized by a sharp spatial discontinuity of the phosphatic horizons and by their rapid wedge-out. Thus, the phosphorite content of the formation described most likely has no practical significance.

The Volcanogenic-Siliceous-Carbonate Phosphorite formation (V- C_1) was distinguished by Mkrtch'yan [8] in a volume of the Tamalyk suite; associated with it is the Tamalyk phosphorite deposit. It is known only in the southwest of the Azyrtal uplift (see Fig. 1). In general, the area of its outcrops extends submeridionally along the strike of the aforementioned Balyksa trough to which it is confined [4]. In a volume taken by us [6], different from the original the volcanogenic-siliceous-carbonate formation is a formation of two end members; its lower part is predominantly limestone, while its upper part associated with phosphorite ores has a

varied volcanogenic-siliceous-terrigenous-carbonate composition. In general, the formation is composed of carbonate (55%), siliceous (30%) and extrusive (10%) rocks. The distinctive characteristics of the formation are determined primarily by black siliceous rocks, which include siliceous, clay-siliceous, calcareous-siliceous, siliceous-calcareous shales and massive cherts [9]. All the rocks are enriched to some degree in carbonaceous material. The productive part of the formation is characterized by frequent interstratification of the enumerated varieties of siliceous rocks, carbonates (mainly limestone and dolomitic limestone) and, in places, extrusive rocks, which forms a highly diversified picture of the irregular vertical succession of components. Most of the lithologic varieties of the section are dark-colored and pyritized. Since a detailed description of the volcanogenic-siliceous-carbonate formation appears elsewhere, we shall not expand on it here. The thickness of the formation is 1100-1800 m.

Studies of the volcanogenic-siliceous-carbonate formation throughout the area of its occurrence have allowed us to draw the following conclusions.

1. The productivity of the formation decreases from the Tamalyk deposit southward.
2. The composition and structure of the formation compared to the section of the Tamlyk deposit change in the same direction: the thickness of the lower, limestone part and the "mottled" structure of the upper productive part decrease; rhythmic succession appears in the formation; volcanogenic rocks disappear from the section.

Correlation of the above characteristics with the disappearance of productive horizons allows us, on the one hand, to consider these aspects as local ore-controlling factors of phosphorite content and, on the other, suggests that the prospects of the formation are limited to the Tamlyk deposit and its immediate surroundings.

The Siliceous-Carbonate Phosphorite Formation (R_3 -V) was distinguished by us in a volume of the Litvinskaya suite [3]. It is confined to the relatively narrow Batenevskaya zone [5], which represents the junction of two paleostructures — the Beloiys-Bellykiskii trough and the Azyrtal uplift (see Fig. 1). Also associated with the position of the zone are the structural features of the siliceous-carbonate formation. Its principal constituents (limestone, dolomite, and siliceous rocks) form, in isolated exposures, any one of a number of combinations both in the quantitative sense and in the cyclical sequence. The largest phosphorite occurrences of the Batenevskii ridge (Yulinsk, Arasynsk, and Bagradsk) are confined to the siliceous-carbonate formation and have been repeatedly described in the literature [2, 11, 12, et al.]. The productive horizons of these occurrences are characterized by a very uneven distribution of the useful mineral and by a discontinuity and rapid wedge-out of the phosphorite beds along the strike direction. These studies of the formation have revealed the extremely uneven distribution of phosphorites over the area and the absence of a clear pattern in the alternation of phosphatic and nonphosphatic sections, although rocks with higher P_2O_5 concentrations have been found everywhere. Also associated with the uneven spatial distribution of the useful mineral may be the low productivity of this siliceous-carbonate complex and the absence, in this connection, of revealed commercial deposits of phosphorite ores.

As is evident from the foregoing, each rock association described has not only its own lithologic characteristics but also its own phosphorite distribution patterns and reveals a definite paleotectonic zoning. Part of the formations are determined by their own local ore control factors; some differences in structural types of phosphorites are to be found (see Table 1). The data presented emphasize the independence of the described formations in terms of metallogeny.

Thus, the phosphorite deposits of the eastern part of the Kuznetsk Alatau include several independent formations of different stratigraphic and paleotectonic position. Spatially they are confined to the large structure of the northeastern strike — the Azyrtal geanticlinal uplift — and to the area where it joins the adjacent intrageosynclinal trough. The section of the Azyrtal uplift, represented by a thick series of conformably superimposed carbonate formations, includes four productive lithocomplexes (see Fig. 2). The position of phosphate ores in the lower part of the stratigraphic column of this structure is controlled by the distribution of the dolomite or essentially dolomite facies whereby two phosphorite formations — siliceous-dolomite (R_3) and dolomite (R_3 -V) — are herein distinguished. Accumulation of the dolomite lithocomplexes occurred over most of the area in an environment of high tectonic stability, while sedimentation conditions were characterized by a great continuity in space and time. The waters of the paleobasin were saturated with phosphorus, which was reflected in

the overall high phosphate content of the deposits; however, significant amounts of phosphorites were observed only in isolated exposures of maximum mobility.

The phosphorite horizons of higher stratigraphic levels, localized in volcanogenic-siliceous-carbonate and siliceous-shale-carbonate formations, reveal a spatial and genetic relation to volcanic processes and — on a broader scale — to tectonic activity in the Late Precambrian and Early Cambrian throughout the Kuznetsk Alatau. The accumulation of these formations, especially the first, occurred in an environment of active sea-floor spreading. The volcanogenic-siliceous-carbonate formation was confined to the margin of the newly formed Vendian-Early Cambrian trough. Such a position was favorable for the formation of fairly large phosphorite deposits.

It follows from what has been said that there existed two levels of phosphate accumulation in the Azyrtal uplift: a lower level, which was associated with dolomite formations of the Charyshtag and Ulugzas suites and an upper level, which included all the other formations. These levels were separated by a stage of deposition of predominantly carbonate non-phosphatic sediments. The siliceous-carbonate formation of the Late Riphean-Vendian was deposited in the axial part of the Batenevskii ridge (Batenevskaya zone) at about the time of the upper phosphate level. However, phosphate accumulation in the Batenevskaya zone ceased by the start of the Early Cambrian at the very time the richest deposits of phosphorites began to be formed in the Azyrtal uplift. The occurrence of phosphorites in the siliceous-carbonate formation has a definite relation to synchronous volcanism within the Beloiyus-Bellykskii intra-geosynclinal trough to the north, while the determining factor in the spatial localization of phosphorite deposits associated with the formation was the position of the Batenevskaya zone at the junction of the uplift and trough [5].

As one can see from these data, a distinctive feature of the globally spatial Late Cambrian-Cambrian epoch of phosphorite formation as it applies to this region is the development of a number of phosphorite formations extended in time and separated by long period non-phosphatic intervals.

It is well-known that productive horizons in commercially exploited phosphorite basins are associated with one formation, which represents a particular variety of formation typical of the given basin [1]; the stratigraphically above and below phosphate series of phosphorite complexes are generally not observed. Consequently, multiple phosphorite formations cannot be considered among the positive factors in the prediction of large phosphorite deposits. However, the current state of the phosphate market is not oriented in the direction of searching solely for "phosphorite giants." Small phosphate deposits may also be of value if they are located in areas with favorable economic geographic conditions. These areas include the eastern part of the Kuznetsk Alatau. New small-scale deposits may be found here in siliceous-dolomite and dolomite formations in areas which are most favorable to phosphate accumulation as well as in unexplored areas of development of the siliceous-carbonate formation. In particular, prospecting operations need to be conducted in the upper course of the Tom' River (Shora River basin) as well as in the zone extending from the upper reaches of the Sora River to the upper reaches of the Uibat River. The volcanogenic-siliceous-carbonate formation directly south of the Tamalyk deposit also warrants careful study. Finally, the potentialities of the Tamalyk deposit itself with respect to finding new deposits of both primary ores and secondary phosphorites have not been exhausted.

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THE ASKAN GROUP OF BENTONITE DEPOSITS (GEORGIAN SSR)

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UDC 552.52(477)

A theory of epigenetic hydrothermal genesis of Askan bentonite deposits is discussed. A genetic relationship of these rocks with a syenite-trachyte subvolcanic Late Eocene complex is demonstrated. The limits of metasomatic zonality are broadened so that it includes the zone of potash feldspathization and the subzone of slightly hydrated mica. A metallization zonality concomitant with metasomatic zonality is described. Hydrothermally altered rocks in near-contact zones of syenite intrusive bodies are compared with their trachytic apophyses.

Askan bentonite deposits are found in the Makharadze district of Western Georgia near Askan Village. They occur at the top of the Middle Eocene volcanic bed (the Guri subsuite of Chidil suite) of the Adzharian-Trialeti folded zone amid trachyandesite tuff and polymictic tuffobrecias and tuffoconglomerates. Several smaller bentonite placers have been discovered near the larger deposits (Tsikhisubani and Vaniskedi).

Askan deposits were discovered and investigated in the 1930s by A. A. Tvalchrelidze with active participation of S. S. Filatov and G. V. Gvakhariya. The high quality and diversity of this raw material make for its wide applications in casting and production of drilling muds, purification of materials in food industry, including wine, vegetable, and animal fats, and as a fodder additive in livestock breeding.

From the very beginning, the genesis of Askan bentonites was the subject of debate. Some authors assumed a hydrothermal origin of these rocks [3-5, 7, 8, 11, 12], while others linked their genesis with exogeneous weathering [2, 10] or halmyrolysis [14]. More recent data [5, 8, 12] and the conclusions based on them refuted the exogenous and halmyrolytic hypothesis of the genesis of Askan bentonite and supported the hydrothermal hypothesis. These facts include the absence of any traces of an upper kaolinitic horizon of humid crust of weathering, substantial sulfidization, distinct metasomatic zonality, and sharp contacts and limited occurrences amid homogeneous trachyandesitic tuffs. The prevalent view was that bentonitic deposits [5, 12] were formed in the course of syngenetic hydrothermal alteration of trachyandesitic ash tuffs in a submarine setting.

Geological Institute, Academy of Sciences of the Georgian SSR, Tbilisi. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 71-87, May-June, 1987. Original article submitted June 20, 1985.

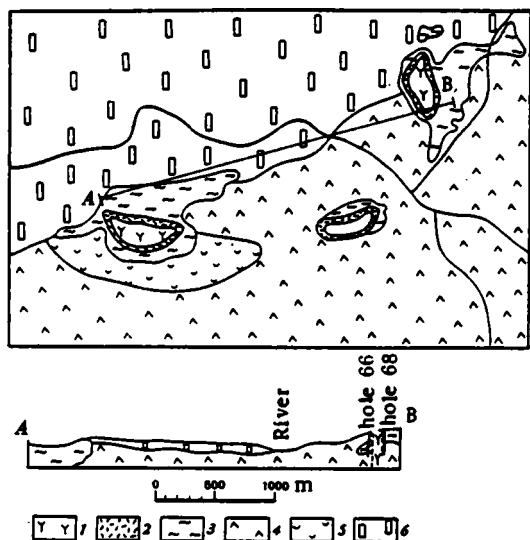


Fig. 1. Geologic scheme of the Askan group of bentonite deposits: (1) potash-feldspathized trachyte (extrusion); (2) micatized rock; (3) bentonite deposit; (4) trachyandesite tuff; (5) mixed trachyte-trachyandesite tuff; (6) polymictic tuff-breccia and tuffoconglomerate.

GEOLOGICAL STRUCTURE AND FORMATION SETTING OF A DEPOSIT

Large bentonite deposits (Tsikhisubani and Vaniskedi) and smaller placers are controlled by trachytic veins and extrusions, cutting across a member of trachyandesitic ash tuff and overlying a bed of polymictic trachybasalt-trachyandesite-trachytic tuffobreccias and tuffoconglomerates, which are the enclosing rocks of Askan bentonite placers (Fig. 1).

Tsikhisubani deposit is one of the largest; it is situated in the gorge of Bakhvitskali River near the ruins of an ancient fortress at Askan Village. The deposit is being mined with the open cast method. It tends to be associated with the contact zone of a potash-feldspathized trachytic extrusion; it is an isometric body 750 m long, from 30 to 260 m thick, traceable by bore holes to a depth of 200 m (Fig. 2).

A zone of micatized rocks up to 30 m thick occurs between the trachytic extrusion and the bentonitic deposit. Three zones of metasomatic alteration are identified in the Tsikhisubani quarry: 1) potash feldspathization zone developed on the trachytic extrusion and confined within it; 2) micatization zone; and 3) montmorillonitization zones. The productive bentonitic deposit encompasses the external part of the micatization zone, which consists of mixed-layer mica-montmorillonitic units, such as rectorite, and a montmorillonitization zone. Recent studies by the Geology Administration of the Georgian SSR and the Caucasian Institute of Mineral Resources determined that potash-feldspathized trachytes are a high-quality feldspar raw material suitable for fabrication of fine ceramics.

On the eastern flank of the Tsikhisubani quarry, overlying the fully bentonitized trachyandesitic ash tuffs, is a small island of bentonitized polymictic tuffobreccias and tuffoconglomerates cut across by apophyses of a trachytic extrusion. It is noteworthy that they contain either fresh or partially altered pebbles immersed in fully bentonitized cement.

In bentonites formed after trachyandesitic tuff, relicts of a primary rock with well-preserved tuff structure and relicts of pumice fragments and biotite crystals are sometimes observed.

The Vaniskedi deposit is situated 2 km to the northeast of the Tsikhisubani deposit and is similar to it in geological structure. The enclosing rocks here are the same trachyandesitic pumice tuffs and polymictic breccias and tuffoconglomerates (see Fig. 1); the bentonitic placer is confined to an extrusion of potash-feldspathized trachytes separated from it by a thin intermediate micatization zone similar to that of the Tsikhisubani deposit. Drilling data reveal a complex isometric pseudostratiform shape of the bentonite placer (Fig. 3). Southeast of the Vaniskedi deposit, in a similar geologic environment close to the contact zone of trachytic veins, small bentonitic bodies up to 5 m thick are found. Somewhat further south, in the gorge of Ochkhamura River, a syenitic subvolcanic intrusion has been discovered. It intrudes into the lower portion of the trachyte-trachyandesitic bed. Its exocontact zone exhibits developed potash-feldspathization and sericitization. Syenites are similar in composition to ore-controlling trachytic veins; the latter are apparently its apophyses.

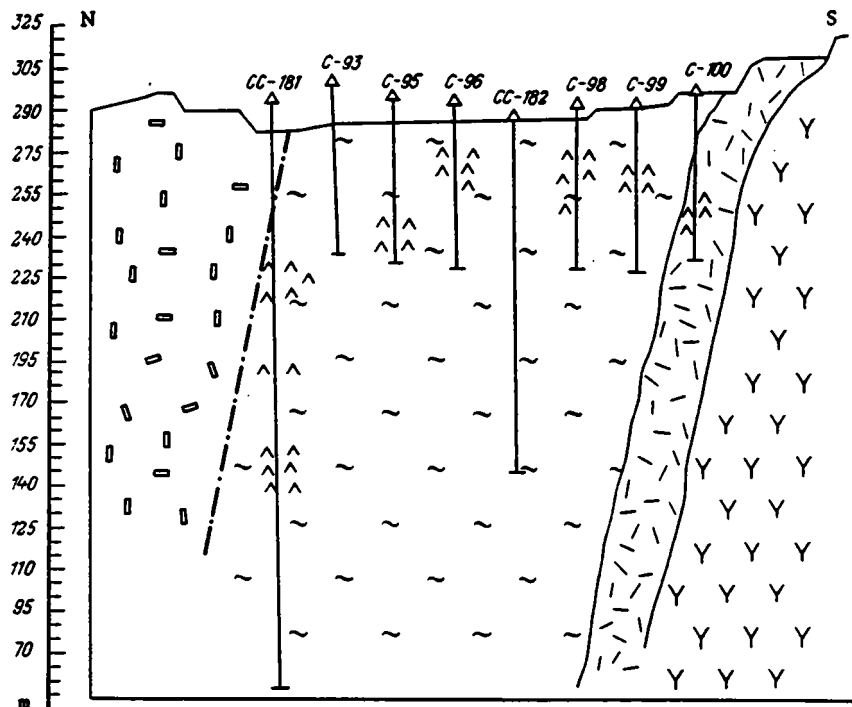


Fig. 2. Geologic profiles based on bore hole cores in the central part and western flank of Tsikhisubani quarry. Dashed line indicates faults. Other notations as in Fig. 1.

Likewise, other trachytic bodies and extrusions seem to be apophyses of syenitic sub-volcanic intrusive masses, widespread in the area. K-Ar absolute datings indicate the same age of these entities* (Table 1): the age of trachytic extrusions ranges from 39.3 to 43.4 million years; the age of syenites is 41.0 million years. They correspond in age also with the bentonitic deposit (39.04 million years), indicating a temporal genetic association of bentonitization and the trachyte-syenitic subvolcanic complex.

Metasomatic alterations associated with syenites are similar in their direction and pattern to processes that tend to correlate with trachytic extrusions. In the near-contact zone of syenitic bodies, a thick zone of potash feldspar metasomatites is widespread; these rocks are succeeded by a zone of micatization and further bentonitization. The argilized zone (bentonitization) associated with syenites, however, is strongly reduced and does not exceed 10 m in thickness, while potash feldspathization and micatization zones are several hundred meters thick. Potash feldspathization can be observed in the exocontact zone of syenites far beyond their limits, whereas in trachytes it is merely an autometasomatic intra-extrusive process. Other mineralogic distinctions also exist and will be discussed later, but the overall pattern of metasomatism also confirms the affinity of these bodies.

Trachytic apophyses of syenitic subvolcanic intrusives cross the uppermost horizons of the Middle Eocene strata, including its topmost polymictic tuffbreccias and tuffoconglomerates. The latter are a regressive facies, as evidenced by diverse composition of pebbles, which include olivinic trachybasalts, trachyandesites, and trachytes; these were products of erosion of different horizons of Chidil suite (Middle Eocene), folded toward the Middle Eocene (the pre-Upper Eocene Trialeti phase, associated with the closure of the Adzhari-Trialeti rift [1]). The Late Eocenic development of the Adzharian-Trialeti zone was characterized by regressive conditions of a shallow sea and islands, confirmed by abundant Late Eocene polymictic tuffosandstones and tuffoconglomerates.

Trachytic extrusions and veins, as noted above, cut across polymictic tuffoconglomerates occurring at the top of the Middle Eocene. The absolute age of syenites, determined by the K-Ar method, their trachytic apophyses, and the bentonite deposits themselves ranges from 43 to 39 million years; according to the radiometric scale of [12], this corresponds to the Upper Bartonian and Lower Priabonian stages, lying at the boundary between the Middle and Upper

*The error of the method is $\pm 10\%$.

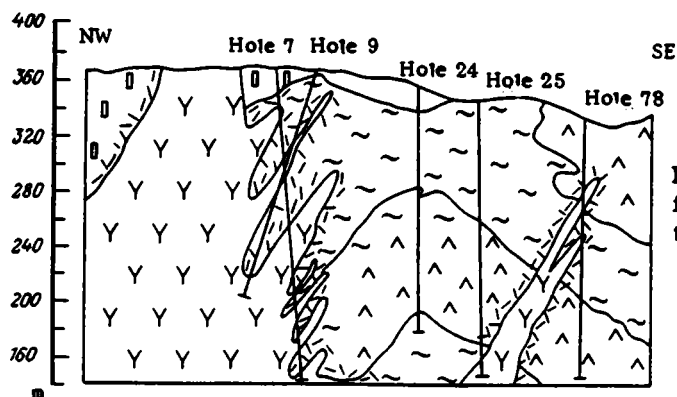


Fig. 3. Geologic profile based on the cores from bore holes in Vaniskedi deposit. Notations as in Fig. 1

Eocene — the time of closure of the Adzharian-Trialeti rift, the shallowing of the sea, and the emergence of islands.

METASOMATIC ZONALITY AND ITS MINERALOGIC CHARACTERISTICS

Three metasomatic zones have been identified in the Tsikhisubani and Vaniskedi deposits: potash feldspathization with areas of albitite micatization, micatization, and montmorillonitization. An earlier study [8] determined the following paragenetic series of authigenic minerals in the Tsikhisubani deposit: hydromica LM + mixed-layer mica-montmorillonite units + montmorillonite (which was an indicator of zonality in the deposit). Within the Tsikhisubani deposit, Mzhaviya [6] discovered a small copper-polymetallic metallization. Later, in 1964, a sulfidized zone up to 1 m thick was exposed in the southeastern flank of the quarry; it is represented by sphalerite-galenite-chalcopryrite-pyrite veinlets [8, 9]. The zone has been fully excavated, but slight pyrite-chalcopryritic and sphalerite-galenitic insets are observed in all three zones identified by us. In the montmorillonitization zone it is reduced substantially and is observed only in its inner portion, being gradually transformed into sulfate mineralization, represented by gypsum and jarosite. Sulfate mineralization also disappears soon, and most of the bentonitic placer contains neither sulfides nor sulfates.

Unlike our predecessors [8, 9], we have expanded the scope of the zonality and, accordingly, the paragenetic series of its indicator minerals represented by the following sequence: potash feldspar + hydromica LM + slightly hydrated mica + mixed-layer mica-montmorillonite formations (rectorite) + montmorillonite. On this basis we have suggested a zonal series expressed in potash feldspathization, micatization, and montmorillonitization. The micatization zone is subdivided into several subzones: hydromica LM, slightly hydrated mica, and rectorite.

The potash feldspathization zone, formed after trachytic extrusions, consists of potash feldspar (mainly monoclinic or with minor triclinicity), quartz, and pyrite. Isolated albitized areas occur sporadically; they consist of albite, quartz, and pyrite. A relict trachyte texture has been retained in potash feldspars and albites. A superimposed sericitization is observed in this zone; it is probably associated with the cooling of the hydrothermal solution at the final stage of the process.

The micatization zone was formed largely after trachyandesitic tuffs, sometimes after polymictic tuffobreccias. The subzones identified by us occur in the following sequence with respect to potash-feldspathized trachytic extrusion and bentonitic placer:

- hydromica LM zone; hydromica LM, quartz, pyrite (galenite, sphalerite, chalcopryrite);
- slightly hydrated mica subzone: slightly hydrated mica, quartz, pyrite (galenite, sphalerite, chalcopryrite); a presence of kaolinite, halloysite, and magnesian chlorite has been established;
- rectorite subzone: rectorite, quartz, magnesian chlorite and pyrite (galenite, sphalerite, and chalcopryrite). In this subzone, the proportion of montmorillonitic layers increases toward the montmorillonitization zone in mixed-layer units; it gradually becomes the montmorillonitization zone.

The montmorillonitization zone was formed after trachyandesitic tuffs and polymictic tuffobreccias; it consists of several subzones, occurring in the following sequence, starting from the boundary with the rectorite subzone:

TABLE 1. Age Determinations of Syenitic Subvolcanic Intrusions, Trachytic Extrusions, and Bentonite Deposits: K-Ar Dating

Specimen number	Specimen characteristics, location	K, %	^{40}K , 10^{-6} g/g	Proportion of radiogenic ^{40}Ar , 10^{-6} cm ³ /g	^{40}Ar , 10^{-6} cm ³ /g	^{40}Ar , 10^{-6} g/g	^{40}Ar , 10^{-3}	Age, million years	Mean age, million years
181	Extrusive trachyte cutting across trachyandesite tuffs near Vaniskedi Village	5,59 5,59	6,67 6,67	42,4 45,0	8,55 8,67	15,30 15,47	2,30 2,32	39,2) 39,5)	39,3 $\pm$ 0,2
158	Potash-feldspathized trachyte; extrusive in Tsikhisubani deposit	11,87 11,87	14,16 14,16	53,7 46,0	19,97 20,51	36,75 36,60	2,52 2,58	42,9) 43,9)	43,4 $\pm$ 0,5
176	A trachyte vein cutting across Middle Eocene trachyandesite tuff near Vaniskedi Village, 0,5 km from Bakhmaro Village	5,16	6,16	42,0	8,02	14,36	2,33	39,7	
152	Syenitic intrusive cutting across rocks of the Middle Eocene bed (Guri subuite) near Gomi Village, exposed on the right side of the road to Bzhuzhi Hydropower Plant	5,69 5,69	6,79 6,79	32,0 18,0	8,64 9,63	15,41 17,25	2,27 2,54	38,7) 43,2)	41,0 $\pm$ 2,2
178	Bentonite from montmorillonitization zone near Vaniskedi	6,47	7,72	53,0	9,99	17,84	2,31	39,0	

Notes. 1. Age values computed from potassium decay constants: $\lambda_K = 0.581 \cdot 10^{-10}$ /year, $\lambda_B = 4.962 \cdot 10^{-10}$ /year. 2. Measurements performed by the Laboratory of Geochronology and Nuclear Research of the Institute of Geology of the Academy of Sciences of the Armenian SSR (director G. P. Bagdasaryan).

TABLE 2. X-Ray Measurements of Hydromica 1M and Mixed-Layer Formations

Sample 85		79		138	
$d/n, \text{\AA}$	l	$d/n, \text{\AA}$	l	$d/n, \text{\AA}$	l
10.28	10	10.05	3	11.95	3
5.01	5	7.69	5	10.16	6
4.25	3	4.75	2	5.00	3
3.95	2	3.71	3	4.48	2
3.70	5	3.60	3	4.25	2
3.62	2	—	—	—	—
3.47	3	3.32	5	3.31	10
3.32	10	3.01	4	2.88	3
3.01	4	—	—	2.71	3
2.90	2	—	—	1.99	3
2.57	3	—	—	—	—

- montmorillonite, rectorite, pyrite (chalcopyrite, galenite, sphalerite);
- montmorillonite, gypsum, jarosite;
- montmorillonite

The sequence exhibits a gradual disappearance of rectorite, the replacement of sulfidic mineralization by sulfatic mineralization, and, finally, the formation of a montmorillonite subzone with no sulfides or sulfates.

We will now describe the metasomatic zonality in terms of the characteristic indicator minerals.

Potash Feldspathization Zone. Potash feldspar consists of two varieties: monoclinic — the characteristic line 2.965 Å (samples 3425, 3418, 3405); and a slightly triclinic variety (0.22) — the characteristic line 2.965 Å (sample 3417).

Micatization Zone. Subzone of 1M hydromica: A phase of pure authigenic 1M hydromica has been described by Rateev and Gradusov [8]. Electronographic measurements have determined the following parameters of the unit cell of sample 207: $a = 5.2$; $b = 9.0$, $\theta = 10.2^\circ$; $\beta = 100^\circ 20'$. Based on x-ray structural, thermic, and IR spectroscopic investigations, it has been shown that hydromica is a micaceous mineral of a dioctahedral type belonging to the muscovite-sericite series.

Based on our x-ray-structural (Table 2), IR-spectroscopic, thermic, and electronographic studies of the fractions <0.001 mm (sample 85) from Tsikhisubani deposit, the exclusively crystalline phase has been confirmed without any noticeable swelling of interlayers ($d_{1n} = 10.28$ Å). It is represented by the hydromica of polytype modification (electronographic investigations were performed by A. P. Zhukhlistov) and is similar to that determined by Rateev and Gradusov [8].

Slightly Hydrated Subzone. Diffractograms of oriented preparations (samples 79, 87, and 89) from the Tsikhisubani deposit indicate the presence of slightly hydrated mica with $d = 10.05$, 10.02 , and 10.05 Å, respectively, (Fig. 4). Electronographic investigations determined a polytype modification 1M + kaolinite (samples 79 and 87) and a mix 1M >> 2M (sample 89).

The differential heating curves of these samples are similar. As an illustration, we present only the thermogram of sample 79 (Fig. 5), which demonstrates the endothermic effect. It corresponds to the removal of adsorbed water at 160°C and 5.75% weight loss, clearly shown in DTG curve. In the average temperature region of the DTA and DTG curves, a dehydroxylation effect is observed which is associated with a weight loss of 5.75%. From 450 to 720°C the DTA curve shows an exopeak, representing the decay of the mineral structure. On the TG curve a small exopeak on the DTG curve reflects a small loss of weight (0.5%). These facts indicate phase transformations typical for a halloysite mineral type.

IR spectra of the fine fraction (sample 79) are represented mainly by lines typical for dioctahedral micaceous minerals. Absorption lines are discernible in areas of 535 , 520 , 1030 , 750 , 800 , and 3620 cm^{-1} , corresponding to valence and deformational oscillations of Si—O—Al^{IV}; Si—O; Si—O; Si—O—Al and other bonds (Table 3). An intensive line at 900 cm^{-1} reflects a low content of octahedral Mg in the crystal mineral composition, which is also confirmed by the chemical composition of the fine fraction (Table 4).

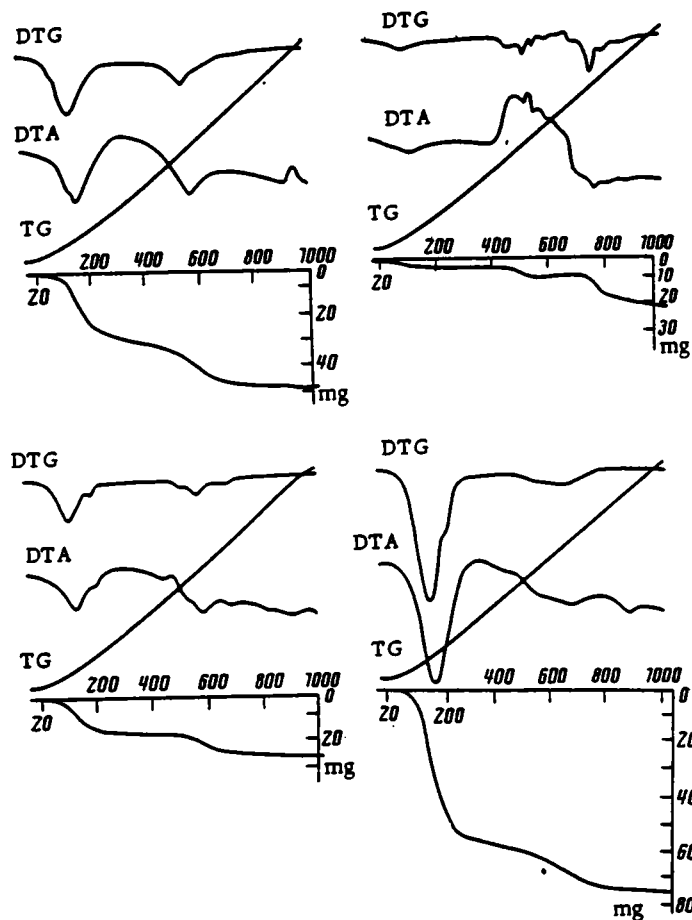


Fig. 5. Differential thermal curves of clay and hydromica minerals (analyst T. V. Batiashvili).

by the chemical composition of its fine fraction (see Table 4). The electronographic investigation of the mica component of sample 141 revealed a polytype modification 1M > 2M, but closer to 1M; in sample 162 the modification 1M was identified.

The differential heating curves of samples 138 and 141 fixed slight endoeffects of weight loss (4 and 5.5%, respectively); in sample 162 the loss was 4.75%. They all exhibited the same differential and the appearance of an exopeak near 420-700°C, reflecting the decay of the pyrite structure (see Fig. 5). IR spectra of absorption of the samples are largely similar (see Table 3), although some distinctions are observed: sample 138 has a line on 700 cm^{-1} ; samples 141 and 162 on 780-800 cm^{-1} . Sample 141 has a slightly discernible line in the 720-780 cm^{-1} area and an arm near 1140 cm^{-1} . All these data indicate a mixed-layer character of these samples.

The diffractograms of samples 119, 121, and 132 from the Tsikhisubani deposit indicate a magnesian chlorite phase in addition to the mixed-layer mica-montmorillonite mineralization (see Fig. 4). A superperiod in the region of small angles ($d > 20$ Å) is discernible; the other reflections are broad; the most intense are reflections in the initial state of sample 119 (10.91 Å), with glycerine (13.07 Å), and after heating (10.05 Å). This mineral is close to rectorite and can be defined as a rectoritelike phase. The diffractogram of sample 121, in contrast to sample 119, distinctively exhibits a superperiod ($d = 25.4$ Å); the most intense lines are characterized by the following values: $d_{\text{in}} = 11.16$ Å, $d_{\text{glyc}} = 13.27$ Å and $d_{\text{calc}}(300^\circ\text{C}) = 10.16$ Å; in the diffractogram of sample 132 these are 10.21, 10.0, and 9.94 Å, respectively. Samples 119 and 121 were collected from bentonitized cement of polymictic tuffoconglomerates of Tsikhisubani deposit; sample 132 from bentonitized trachyandesitic tuff.

Differential curves of samples 121 and 132 are similar (see Fig. 5); they exhibit a pronounced endothermic effect of removal of adsorbed water at 150°C, associated with a 5% weight loss. In the medium-temperature interval (500-700°C), DTA and DTG curves reflect a dehydration

TABLE 3. Frequencies of the Main IR Absorption Bands

Sample number	Si—O	Si—O	Si—O—Al ^{VI}	Si—O—Si	Si—O—Al	Me—OH ⁺	Si—O	OH
79	440	475	535		840	920	1030	3620
141	430	480	540—585		—	—	—	—
162	430	480	525—585	780—800 duplicate	880	920	1030	3620
138	430	480	535	780—800 duplicate	830	920	1030	3620
121	440	480	535		830	920	1030	3620
119	440	480	535		830	920	1030	3620
140	430	470	525		840	920	1030	3620
163	430	470	525		840	920	1030	3620

Note: Analyst T. A. Gvakhariya.

TABLE 4. Chemical Composition of Fraction <0.001 mm

Sample number	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	Σ
79	45.55	0.49	21.83	2.17	2.10	2.73	0.14	2.29	0.05	3.70	4.60	10.30	96.01
119	46.67	0.46	25.50	0.70	3.15	5.34	—	1.52	0.70	3.50	2.90	8.10	99.56
121	47.12	0.46	24.55	1.18	3.15	5.31	—	2.16	0.20	3.80	3.64	8.28	99.85
132	50.22	0.34	21.83	1.91	2.62	5.21	—	2.06	0.10	4.00	3.66	7.88	99.83
141	56.64	0.46	20.23	0.47	2.10	2.22	—	3.28	3.00	5.00	0.86	5.80	100.06
162	52.57	0.50	25.84	1.70	1.13	1.87	—	1.63	0.10	5.50	2.20	7.04	100.08
163	49.96	0.40	16.73	3.79	0.79	4.92	—	2.93	0.05	0.80	9.74	9.84	99.94

with an additional 2.5% weight loss. A slight endoeffect in the interval of 920–950°C represents the removal of the remaining hydroxyl water and complete decay of the structure with a further 1% weight loss.

The IR spectrum of sample 121 presents no distinctive lines of valency or deformational fluctuations.

Montmorillonitization Zone. X-ray investigation of samples 137 and 140 from Tsikhisubani and samples 163 and 168 from Vaniskedi indicate a natural continuation of the micatization into the montmorillonitization zone. The x-ray patterns of samples from Tsikhisubani deposit are identical (see Fig. 4): they represent a phase similar to montmorillonite, but with small $d_{1n} = (10.28 \text{ \AA})$; $d_{glyc} = 16.9 \text{ \AA}$ $d_{calc} = 9.85\text{--}9.87 \text{ \AA}$. The x-ray patterns of samples from the Vaniskedi deposit present more typical montmorillonites. They differ from the former by a larger d_{1n} (~14 Å), which is probably due to different interlayers, where bivalent cations are predominant; this is also confirmed by a high content of CaO (2.93%) in the fine fraction of sample 163 (see Table 4).

The differential curves of these samples are identical (see Fig. 5). They are highly hydrated, with a large weight loss, 68.8 (17.2%) and 87.0 m/g (21.75%), confirming their typical montmorillonitic nature.

The different methods of mineralogic analysis thus indicate that an autometasomatic zone of potash feldspathization after trachytic apophyses was followed by a micatization zone with several subzones: 1) dioctahedral hydromica 1M; 2) slightly hydrated mica; and 3) rectorite, gradually passing over into montmorillonitization zone. In the micatization zone, mixed-layer minerals of a rectorite type with a tendency to regular alternation of hydromicaceous and montmorillonitic packets gradually increases; the role of the latter packets progressively rises, as has been reported in [8], attaining the maximum in the montmorillonitization zone.

Besides the typomorphic mineral associations described above, relicts of parent rocks with residual minerals of magmatic and syngenetic hydrothermal genesis are found in the micatization and montmorillonitization zones. The residual effusive minerals include relicts of biotite and plagioclase crystals; relicts of primary texture of trachyandesitic tuffs with preserved glass and pumice fragments are found. Of the residual minerals of a hydrothermal origin, the more frequent are zeolites — analcime and natrolite. Their presence in bentonitized tuffs has been described in earlier publications [5, 12]. Zeolitization is widespread in the parent rocks of bentonitic deposits, the trachyandesitic tuffs that were not

TABLE 5. Chemical Composition of Metasomatites Associated with Trachytic Apophyses of Syenite Intrusions and Results of Recalculations of the Migration of Components by Using the Atomic Volume Method

Oxide	I	II	III	IV	V	VI	Atom	II	III	V	VI
SiO ₂	59,52	64,5	72,30	59,79	51,51	53,92	Si	11,16	31,60	-27,95	-27,92
TiO ₂	0,34	0,36	0,27	0,34	0,31	0,28	Ti	0,04	-0,19	-0,12	-0,27
Al ₂ O ₃	19,95	17,2	14,42	18,96	20,81	15,57	Al	-7,22	-14,55	1,73	-15,20
Fe ₂ O ₃	2,37	1,47	0,51	1,74	2,22	1,40	Fe ³⁺	-2,28	-4,68	5,82	-1,46
FeO	0,70	0,12	1,22	0,67	1,82	2,10	Fe ²⁺	-1,45	1,24	2,63	2,69
MnO	0,17	—	—	0,35	0,11	—	Mn	-0,43	-0,43	-0,62	-0,88
MgO	1,67	0,63	0,14	1,30	2,58	4,12	Mg	-2,62	-3,89	2,85	5,31
CaO	3,19	0,3	1,20	4,12	1,10	1,95	Ca	-7,24	-5,04	-7,73	-6,28
Na ₂ O	4,21	0,46	8,00	2,35	0,05	1,50	Na	-9,39	9,07	-5,78	-2,78
K ₂ O	6,26	14,1	0,80	4,73	6,50	1,30	K	19,22	-13,69	3,54	-9,17
P ₂ O ₅	0,46	0,5	—	—	—	—	O	1,25	17,26	-98,49	-135,94
H ₂ O ⁻	—	—	—	2,73	—	—	OH	-0,12	0,59	8,03	13,15
H ₂ O ⁺	—	—	—	1,46	—	—	—	—	—	—	—
Loss to heating	1,00	0,9	1,26	—	4,80	10,18	Balance	0,9?	22,39	-115,23	-177,95
H ₂ O	0,16	0,22	—	—	8,32	7,16	—	—	—	—	—
Sum	100,2	100,76	—	98,54	—	—	—	—	—	—	—
dv	2,50	2,48	2,45	2,51	2,37	2,08	—	—	—	—	—

Notes. I) Fresh trachyte (initial sample 579); II) potash feldspar (altered sample 22); III) albitite (altered sample 112); IV) trachyandesitic tuff (initial sample 121); v) micatization zone (altered sample 79); VI) montmorillonitization zone (altered sample 140).

TABLE 6. Chemical Composition of Metasomatites in the Contact Zone of Alteration of Syenite-Monzonite Subvolcanic Intrusions and the Results of Recalculation of the Migration of Components with Atomic Volume Method

Oxide	I	II	III	IV	V	VI	Atom	II	III	IV	V	VI
SiO ₂	59,79	60,90	62,55	61,50	59,45	40,79	Si	5,23	3,18	-3,08	-24,04	-42,79
TiO ₂	0,34	0,30	0,40	0,52	0,40	0,50	Ti	-0,13	0,13	0,30	0	0,47
Al ₂ O ₃	18,96	16,78	18,10	21,32	23,36	18,54	Al	-4,80	-3,24	3,36	1,93	1,17
Fe ₂ O ₃	1,74	3,52	3,22	1,65	0,93	11,19	Fe ³⁺	4,61	3,52	-0,43	-2,40	25,06
FeO	0,67	0,36	1,08	1,31	0,70	2,70	Fe ²⁺	-0,76	0,97	1,45	-0,20	5,42
MnO	0,35	Traces	0,07	—	—	0,18	Mn	—	-0,71	—	—	-0,41
MgO	1,30	0,30	1,67	0,86	1,54	4,13	Mg	-2,49	0,83	-1,20	0	7,60
CaO	4,12	0,67	1,22	1,64	1,18	14,91	Ca	-8,63	-7,35	-6,42	-7,84	28,87
Na ₂ O	2,35	1,40	9,60	0,20	0,30	1,00	Na	-2,33	17,62	-5,42	-8,25	-1,69
K ₂ O	4,73	15,00	0,80	4,50	4,60	1,00	K	26,38	-9,91	-1,11	-2,11	-9,24
P ₂ O ₅	—	0,26	0,26	—	—	0,37	O	2,93	6,23	-13,17	-61,40	-6,86
H ₂ O ⁻	2,73	—	—	—	—	—	OH	-9,13	-8,30	4,78	5,05	-0,78
H ₂ O ⁺	1,46	—	—	—	—	—	Balance	5,05	7,06	-38,51	-96,27	6,23
H ₂ O	—	0,20	0,10	0,60	0,84	0,38	—	—	—	—	—	—
Loss to heating	—	0,34	0,80	5,80	6,50	3,32	—	—	—	—	—	—
Sum	98,54	100,04	99,87	99,90	99,80	99,61	—	—	—	—	—	—
dv	2,51	2,55	2,45	2,39	2,12	2,63	—	—	—	—	—	—

Notes. I) Trachyandesitic tuff (sample 121); II) potash feldspar (sample 572a); III) albitite (sample 3493); IV) micatization zone (sample 150); V) bentonitization zone (sample 160); VI) epidosite (sample 3468); sample 121) initial; others altered.

montmorillonitized, and polymictic tuffobreccias located far beyond the deposits. In addition, polished sections reveal a substitution in polymictic tuffobreccia of analcime cemented by montmorillonite-hydromicaceous masses.

In the western Adzharia-Trialeti, the upper horizons of the Middle Eocene strata exhibit a characteristic syngenetic regional zeolitization [4]. On this basis we assume that zeolitization caused by a regional hydrothermal process; hydrothermal processes of bentonitic deposits, however, are local and superimposed on zeolitized rocks.

PETROCHEMICAL ANALYSIS OF ZONALITY

The metasomatic zonality of Tsikhisubani deposit, traced from the hydromica LM zone through the rectorite to montmorillonitization zones, is accounted for in [8] by a deficit of potassium in this direction. The decline of potassium activity in the hydrothermal process in the direction from the potash feldspar zone to the montmorillonitization zone in an even wider range is traced and confirmed by our data (Table 5). Rubidium, which is coherent to potassium, behaves similarly; its contents in potash feldspar is 0.036%, in the micatization zone from 0.011 to 0.019%; in the montmorillonitization zone, it drops to 0.004%. The pattern of silica migration is also indicative; its deficit is traced parallel to that of potassium from the potash feldspar to the montmorillonite zone (see Table 5). A significant loss of silica is observed in the latter zone. The process is characterized in general by a removal of the basic petrogenic elements, except for the influx of silica and potassium in the potash feldspathization and micatization zones (Table 6). In albitites an influx of sodium is observed due to the loss of potassium; in the micatization and montmorillonitization zones a certain inflow of magnesium is noted.

The Tsikhisubani deposit exhibits a similar ore zonality: in potash feldspars, pyrite is predominant; in the micatization zone, chalcopyrite, galenite, and sphalerite appear along with pyrite. This association is further traced at the beginning of the montmorillonitization zone. As noted, a small copper-polymetallic metallization has been discovered in the Tsikhisubani deposit. The formation of chalcopyrite veinlets is probably associated with lixiviation and redeposition from copper-infested trachyandesitic tuffs containing 200 g/ton of metal in the course of their micatization and montmorillonitization. Copper contents in these zones is at most 10-12 g/ton [4].

The transition of sulfidic mineralization to the sulfatic form — gypsum and jarosite — is probably due to the rise of oxygen fugacity. The gradual depletion of sulfate mineralization is due to the dilution of hydrothermal solutions by groundwaters and an abrupt drop of hydrogen sulfide concentration.

COMPARISON OF THE METASOMATIC ZONALITY OF SYENITE INTRUSIONS AND THEIR TRACHYTIC APOPHYSES

As has been mentioned, the metasomatic zonality associated with syenite intrusions differs in certain mineralogical and petrochemical features from the zonality associated with trachytic apophyses, despite the generally uniform directions and similarities.

Syenite intrusions exposed in the gorges of Bzhuzhi and Natanebi Rivers near Gomi, Shemokedi, and Vakidzhvari Villages are characterized by intraintrusive autometasomatic potash feldspathization and albitization, appearing in the form of perthitization and antiperthitization. Quartz-feldspathic metasomatites are widespread on the endocontacts of these bodies and after their enclosing trachytoids of the Guri subsuite. They consist of potash feldspathites and albitites; potash feldspathites are more common, while albitites tend to occur in fracturing zones of the potash feldspathite halos. Small nests (0.5 m) and isometric bodies formed of epidotes are found in quartz-feldspar metasomatites, at a distance from the intrusive body, is succeeded by a micatization zone; the latter gives way to an argillization zone with participation of rectorite and montmorillonite. The latter zone is greatly reduced compared with the bentonite deposits described earlier. These zones have the following mineral compositions.

1. Quartz-feldspar metasomatite zone: (a) potash feldspathite subzone: potash feldspar (monoclinic or with minor triclinicity), quartz, biotite (in a sharply subordinate amount), and pyrite; superimposed minerals: chlorite, cerisite, hydromica; (b) albitite subzone: albite, quartz, pyrite; superimposed minerals: chlorite, sericite, hydromica; and (c) epidote subzone: epidote, actinolite, prehnite, chlorite, albite, and pyrite (with a strong epidote predominance).

2. Micatization zone: quartz, pyrite (chalcopyrite, galenite, and sphalerite); electronographic study (sample 159) identified a phase of hydromica 2M1 >> 1M + kaolinite.

3. Bentonitization zone: rectorite, montmorillonite, quartz, kaolinite, and pyrite; an electronographic investigation (sample 160) identified a phase of hydromica 2M1 + kaolinite.

Potash feldspathization was accompanied by an inflow of potassium and an outflow of other petrogenic elements; albitites indicate an increase in sodium against the background of general lixiviation; for epidotes a prevalence of inflow over outflow is characteristic (see Table 6), and formation of trachytoids lixiviated in the process of quartz-feldspar metasomatism in the redeposition zones of titanium, aluminum, iron, manganese, magnesium, and calcium. Micatization and argillization zones were formed with a potassium deficit in solutions, as compared with potash feldspathization, similar to processes in bentonitic deposits.

Sulfide mineralization, represented by pyrite-chalcopyrite-galenite-sphaleritic ore zones, is associated with syenite intrusive bodies. The most significant of them is situated in the near-contact halo of hydrothermal alteration of the syenite body of Korisbude settlement.

Potash feldspathization and albitization are not seen outside trachytic extrusions in bentonitic deposits. Potash feldspar, however, both in the contact zone and in potash-feldspathized trachytes, is represented by the monoclinic variety (line 2.99 Å) or has a low (0.22) degree of triclinicity, with characteristic line 2.966 Å. Epidotes have not been found in bentonitic deposits. The zone of micatization of near-syenite intrusions is represented by hydromica polytypes 2M1 and 1M; kaolinite is diagnosed in minor amounts. The argillization zone of near-syenitic halos is reduced compared with the rectorite subzone and montmorillonitization zone in Tsikhisubani and Vaniskedi deposits. Rectorite, hydromica 1M, montmorillonite, kaolinite, and quartz coexist there. Rectorite is predominant; there is no pure-line montmorillonite subzone, typical for bentonite deposits. In the syenite micatization zone, copper-polymetallic metallization occurs which is similar to that of Tsikhisubani in genesis and composition; sulfate mineralization, however, is absent.

DISCUSSION

Askan bentonite deposits are controlled by trachyte apophyses of syenite-monzonite subvolcanic intrusives. The age of bentonite deposits, as well as of the entire trachyte-syenite-monzonite subvolcanic complex, is from the end of the Middle Eocene to the beginning of the Upper Eocene (43-39 million years).

The proponents of the hydrothermal hypothesis postulate a syngenetic genesis of these deposits and trachyandesitic tuff. However, we are more inclined toward the theory of epigenetic origin of the principal bentonite deposits. The main argument adduced for syngenetic montmorillonitization [12] is that bentonitization stays within trachyandesitic ash tuff. Polymictic tuffobreccia and tuffoconglomerates, which overlie the bentonite deposit conformably, according to these authors, were formed after the deposit was formed. In the last few years, however, bentonite deposits were discovered in polymictic tuffobreccias and tuffoconglomerates; in the eastern flank of Tsikhisubani quarry, bentonitized polymictic tuffoconglomerates have been found with fresh or partially altered pebbles against the background of a fully bentonitized groundmass, cut across by trachytic apophyses.

Bentonitization took place in subaerial environments of islands, produced by Trialeti orophase as a result of closure of the Adzharian-Trialeti rift at the end of the Late Eocene. The complex isometric shape of bentonite deposits, sometimes cutting across the surrounding rocks and sometimes pseudostratiformal, could be attributed to hydrogeologic conditions. An important factor in their formation was groundwater, heated and activated by emanations from syenite-trachyte subvolcanic bodies — subhydrothermal solutions, as defined by Naboko [7]. A subaerial genesis of bentonite deposits is supported by the high fugacity of oxygen, responsible for the succession of sulfide mineralization by sulfate mineralization (gypsum and jarosite) in bentonite deposits.

The shallowing of the sea and the development of a landmass starting from the end of the Middle Eocene in the place of Adzharian-Trialeti trough are evidenced by the presence of polymictic tuffosandstones and tuffoconglomerates, containing materials from different horizons of the Middle Eocene strata.

Syngenetically zeolitized rocks were subjected to bentonitization. Relicts of zeolite mineralization in bentonites were reported earlier [5, 12] and confirmed by our data. There

are also instances of montmorillonitization of the analcime cement of polymictic tuffoconglomerates whose syngenetic origin is beyond doubt.

The Guri subsuite of the Middle Eocene is subject to syngenetic regional zeolitization and low-temperature propylitization [4]. At a distance from trachyte extrusions and bentonite deposits, their enclosing rocks (trachyandesite tuff and polymictic tuffobreccia and tuffoconglomerate) did not experience montmorillonitization. All these observations indicate that the large bentonite deposits are epigenetic hydrothermal formations; zeolitization in western Adzharia-Trialetia is syngenetic to the volcanoclastic deposition process.

We have expanded the range of metasomatic zonality in Askan bentonite deposits described by Rateev and Gradusov [8] by including into it the high-temperature potash feldspar zone formed after trachyte extrusions. We have suggested a more detailed subdivision of the micatization zone, identifying a subzone of slightly hydrated mica. In addition, mineral zonality within deposits corresponding to metasomatic zonality has been identified. The potash feldspar zone is associated with pyritization; the micatization and montmorillonitization zone with pyrite, and chalcopyrite-galenite-sphalerite insets in the montmorillonitization zone, which later is transformed into sulfate mineralization (gypsum and jarosite).

We disagree with the view presented in [5] that the process should be subdivided into syngenetic (montmorillonitization) and epigenetic (hydromicatization and sulfide metallization) phases, which assumes that hydromicatization and sulfide metallization were superimposed upon the bentonite deposit. This hypothesis is contradicted by frequent relicts of trachyandesite tuffs and trachytes in hydromicatized rocks and the regular transition from micatization zone to montmorillonitization zone with a gradual increase of montmorillonite layers in the mixed-layer mica-montmorillonite formation and their transformation into a pure-line montmorillonite.

In following Rateev and Gradusov [8, 9], we consider the relationships of micatization and montmorillonitization to represent a zonality produced by the cooling of a solution with the increasing deficit of potassium from the potash feldspathization zone to the zone of montmorillonite alteration.

A common direction and pattern of hydrothermal processes and zonality have been determined in the contact zone of syenite intrusions and their trachyte apophyses, indicating the existence of a common magmatic source for syenite intrusions and trachyte extrusives. Their affinity is confirmed by similarities of copper-lead-zinc metallization. Significant differences have also been shown in the mineral composition of the zonality and the reduced argillization zone of syenitic bodies, as compared with bentonite deposits of their trachytic apophyses. The differences are explained by different physical and chemical parameters of the process because of the difference in the occurrence depth and the heat reserve of syenite and trachyte extrusions, producing stable high-temperature conditions in the halo of syenite bodies. The large scale of bentonitization in the top structural stories was probably due to the contribution of activated emanations and groundwater warmed by endogenous heat (subhydrothermal solutions) to the hydrothermal process.

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TONSTEINS OF THE IRKUTSK BASIN

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UDC 552.52(571.9)

Kaolinitic and montmorillonitic tonsteins, described in the coal seams of the Irkutsk Basin, are of two types: cryptocrystalline and coarse-grained. A lithological description and identifications of clay minerals are given. It has been established that the source of clay matter of kaolinitic tonsteins was pre-Jurassic kaolinitic crusts of weathering; montmorillonitic tonsteins developed from the crusts of weathering on Siberian traps.

Although the lithology of the Jurassic continental sediments in the Irkutsk Basin has been studied exhaustively, extremely little is known about the occurrence of tonsteins. The available data are limited to the mention of a 0.03 m thick interlayer described by Chekin [17] in the lower portion of the coal seam of the Cheremkhovo deposit. The composition of this interlayer has not been studied, and it remains unclear whether it is indeed tonstein or an ordinary polymineral clay reported in this basin already in the last century [16]. The knowledge of the composition and occurrence of tonsteins in the Jurassic of the Irkutsk Basin is thus so limited that one can think that these lithologically valuable rocks in this area occur sporadically, if at all. Despite the differences in the views of tonstein genesis [12], however, there are premises for finding them in the sediments of this basin.

Investigations in Azeisk and Cheremkhovo deposits have identified a series of tonstein interlayers in coal seams, indicating the widespread presence of these remarkable entities in the Irkutsk Basin. It was discovered at that time that tonsteins in these deposits are represented by different mineral classes, rather than being homogeneous. The present article analyzes the new data to describe the lithology, mineral composition, and distribution in coal seams of tonstein interlayers; conclusions are drawn concerning the genesis of these rocks.

The Jurassic of the deposits studied are similar in their lithology and facies; this is due to their being confined to a zone on the platform side of the basin [1]. The coals of these deposits vary in their degree of metamorphism (brown coals at Azeisk and gas coals

All-Union Scientific-Research Institute of Geologic Exploration and Coal, Rostov-on-Don. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 88-98, May-June, 1987. Original article submitted June 18, 1985.

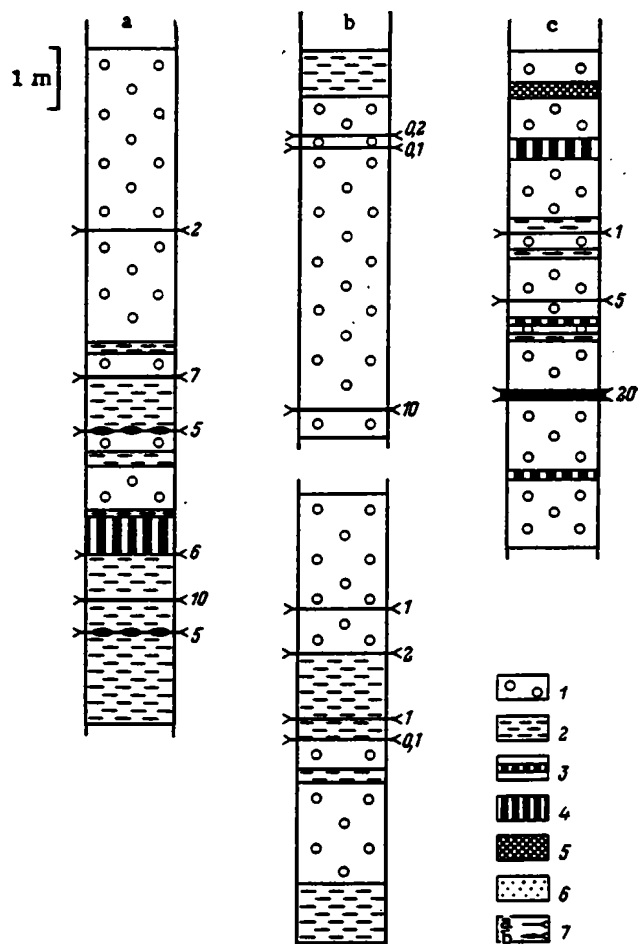


Fig. 1. Distribution of kaolinite tonstein interlayers of various sections (a, b, c) of the coal seam of Azeisk deposit: (1-2) coal (1 - homogeneous massif, 2 - striated-banded); (3) siltstone; (4) coaly argillite; (5) horizon of coaly silic lenses; (6) sandstone; (7) tonstein interlayers (a - consistent thickness; b - rosarylike). Numbers indicated give the thickness in cm.

at Cheremkhovo), although the temperature range corresponding to this metamorphism interval (70-90°C) [10] could not have affected the stability of the initial clay minerals. The parageneses of clay minerals in these tonsteins must therefore either be primary or consist of inherited units [12].

METHODS

The peculiarities in the development and composition of tonsteins require a thorough analysis of specimens in the field, as well as in the laboratory. The morphology of interlayers and their interrelations with coal macrotypes have been described in quarry outcrops; the structures of clay matter were determined, and the degree of homogeneity of interlayers was evaluated by visual inspection. Laboratory investigations consisted of the conventional set of procedures used in clay rock studies. Clay minerals were identified with standard x-ray investigations of the fraction <0.001 mm in an air-dry state and in glycerine-treated specimens, and also by thermal analysis. Chemical analyses were done with x-ray fluorescence; only FeO was determined chemically.

LITHOLOGY AND MINERAL COMPOSITION OF TONSTEINS

The tonsteins of these deposits are specific clay interlayers associating with coal seams. Visual inspection reveals different textures, pigmentation and lithification degree of the clay mass, a sign of structural and mineral diversity. According to the predominant clay mineral, kaolinitic and montmorillonitic tonsteins are distinguished.

In each deposit all the tonsteins are of the same composition, with minor textural variations.

Kaolinitic Tonsteins. This is the most widespread type in different basins; these tonsteins have been studied better than the other type. The familiar petrographic-typological and genetic classifications [6, 18, 21, 23] have been developed for kaolinitic tonsteins.

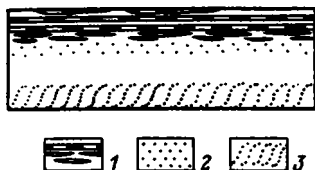


Fig. 2. Details of the structure of kaolinite tonstein interlayer; (1) thin stripes and lenslets of coal; (2) massive tonstein; (3) small oblique (S-shaped) stratification.

Kaolinitic tonsteins in the Irkutsk Basin were discovered for the first time in the Azeisk deposit; there they form up to seven interlayers, localized in coal seams I and II (Fig. 1). In their mineral composition and texture they are similar to tonsteins from other basins [6, 24] but have some unique features. Since these tonsteins are being described for the first time, we will give their detailed characterization.

Kaolinitic tonsteins of the Azeisk deposit are easily discernible by their characteristic light-gray color with a slightly brownish shade. Despite the low degree of coal metamorphism (BZ grade), these tonsteins are lithified, compact, and do not disintegrate in water. The slight differences between them are only in the texture of the kaolinitic mass. According to the classification developed in [5, 21, 23], the kaolinitic tonsteins are divided into two groups: granular and cryptocrystalline.

The cryptocrystalline kaolinitic tonsteins form most of the interlayers; granular varieties have been found in just one, where they are in association with cryptocrystalline. The latter appear as a dense uniform clay mass which contains as a mechanical admixture small fragments and fine dust of a coaly matter; at the base of some of the interlayers this matter produces a typical oblique lamination with small S-shaped layers (Fig. 2). The tops of the interlayers often exhibit thin strips and lines of sapropel coal. Pure coal-kaolinitic interlayers are described, where the thin interstratification of kaolinitic and coaly strips and lines gives rise to a characteristic lined structure.

Cryptocrystalline kaolinitic tonsteins are optically isotropic or react very weakly to polarized light (Fig. 3a). Schüller and Höhne [28] have identified them under the name of "dense tonsteins," this term is commonly used by Soviet lithologists. Recently, Zaritskii [7] suggested the term "cryptocrystalline" for tonsteins with the hidden texture of kaolinitic groundmass. Cryptocrystalline kaolinitic tonsteins of a perfectly homogeneous composition are rare, but most specimens contain an admixture of angular grains of quartz, kaolinized feldspar, and biotite. The grains measure at most 0.2 mm across. Of the minerals in the heavy fraction, apatite and zircon have been reported.

The cryptocrystalline kaolinitic mass has a slightly brownish pigmentation, which is the primary color of the clay mass. Near coal strips the mass becomes decolorized due to reduction of oxide iron during diagenesis [14]. The refractive index of the isotropic mass is 1.550.

The group of granular tonsteins is represented by just one type: a coarse-grained kaolinitic tonstein forming most of the interlayer. Gradual transitions to cryptocrystalline forms are observed only in the near-contact portion.

Coarse-grained kaolinitic tonsteins include two forms of kaolinite. The predominant form appears as granules of variable size up to 0.8 mm. They consist of highly homogeneous very thin platelets of colorless kaolinite with low interference colors. The aggregate pattern of the micrograins of kaolinite in different granules is strikingly similar. Kaolinites of the pre-Jurassic residual crusts of weathering are of a similar structure; they are widespread in the basin and occur beneath the Jurassic sediments [3, 17, 19]. The granules are of an elongate (Fig. 3b), isometric, or irregular shape (see Fig. 3c); with crossed nicols they resemble flakes with a directive orientation coincident with the lamination.

The distribution of the granules endows these tonsteins with a typical silt-psammitic texture (see Fig. 3c), easily recognizable in polished sections with the naked eye.

The second form is cryptocrystalline kaolinite, making up the groundmass. It is identical in texture to kaolinite of cryptocrystalline kaolinitic tonsteins; the brownish nearly isotropic mass is the matrix for smaller scattered grains of quartz, illite flakes, minerals of the heavy fraction (apatite and zircon), and coaly matter. These minerals are found exclusively in the mass of cryptocrystalline kaolinite; they are absent in the kaolinite of the granules. Single larger grains (up to 1 mm) of kaolinized feldspar and elongate kaolinite crystals (pseudomorphoses after mica) are also present, but a genuine crystalline pseudomorphous type of kaolinitic tonsteins [23] has not been found.

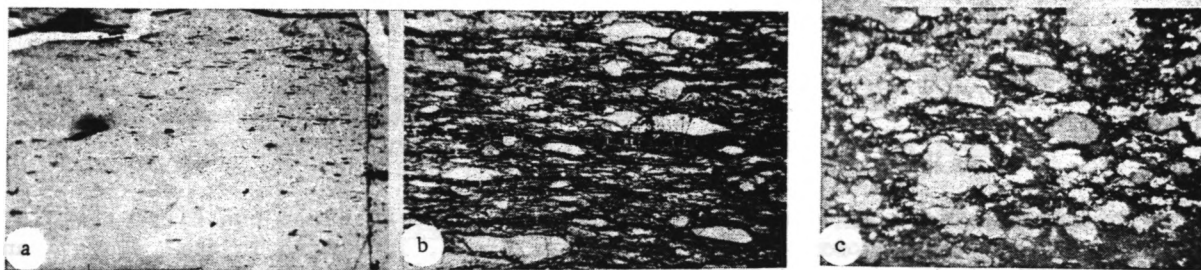


Fig. 3. Kaolinitic tonsteins: (a) cryptocrystalline; (b) coarse-grained with elongate granules; (c) coarse-grained with irregular and isometric granules (silt psammitic texture). Magnification $\times 80$ without analyzer.

A few words should be said about the minerals of the heavy fraction. Apatite is present mainly as irregularly shaped fragments; short-prismatic shapes are observed in rare grains. Zircon is achromatic in short-columnar grains with smoothly rounded pyramid vertices. Apatite and zircon are typical components of a terrigenous-mineralogic association of the Cheremkhovo suite [9], which contains the coal seams.

Coarse-grained kaolinitic tonsteins by their texture and morphology of the granules can be placed with a group of lithoclastic psammites, in which granules represent clastic sand matter and cryptocrystalline kaolinite mass is the cement.

X-ray structural investigations determined a substantially kaolinitic composition of the clay fraction (Fig. 4). The distinct integral basal reflections 7.14 (001) and 3.56 kH (002) diagnose kaolinite, and the presence of weak lines 4.38 (110) and 4.20 kH (111) suggests a low degree of ordering of the structure of this mineral [13]. Illite is identified by a weak reflection 10 kH in glycerine-saturated specimens. The main standard reflections 7.95 and 3.95 kH determine heulandite; its presence is responsible for the relative increase of CaO content in the samples (see Table 1). This mineral usually is found as products of devitrification of volcanic glasses and tuffs and also in andesite and diabase [4]. Although such material has not been found in tonsteins, its contribution to the parent matter of tonsteins should not be ruled out.

Differential heating curves reveal typical thermal effects of kaolinite (Fig. 5); the gentle endothermic peak in the low-temperature region supports the poor ordering of the texture [8].

The compositions of the kaolinite tonstein samples are given in Table 1. The numerical data show that cryptocrystalline and coarse-grained kaolinitic tonsteins are identical in their chemical composition and are similar to kaolinite in SiO_2 and Al_2O_3 contents.

The silicic ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is stable; in only one case a low value of this parameter (0.98) is noted, apparently associated with the presence of gibbsite, although this mineral has not as yet been determined among pre-Jurassic residual weathering crusts [2].

Montmorillonitic Tonsteins. The notion of a tonstein is usually associated with a submonomineral kaolinitic composition of intercoal interlayers. It was only recent that Burger [24] identified montmorillonitic and illitic tonsteins, as well as kaolinitic varieties. These tonsteins are much more rare than kaolinitic ones and are less studied.

In Irkutsk Basin, montmorillonitic tonstein interlayers occur in Cheremkhovo deposit; they are localized in the various parts of the Glavnyi coal seam profile (Fig. 6). The greenish-gray clay mass is of a uniform structure, compounded in isolated interlayers by evenly distributed white kaolinite insets. Unlike kaolinitic varieties, montmorillonitic tonsteins are slightly lithified, although their enclosing coals were metamorphosed in the bituminous stage. Remarkably, none of the clay mass of the interlayers contains coaly matter, but exhibits massive structure or highly indistinct stratification. The contacts with coal are sharp, while kaolinitic tonsteins occur with more gradual transitions.

The absence of an integral sequence in the series of reflections 00 ℓ is a sign of a polymineral composition of the clay fraction. The dominant component is monmorillonite, combined with small amounts of other clay minerals in a mechanical mix.

Montmorillonite is identified by a sharp basal reflection 13 and 14.2 kH in an air-dry state. After glycerine saturation, the peak is shifted to the standard value, 17.8 kH.

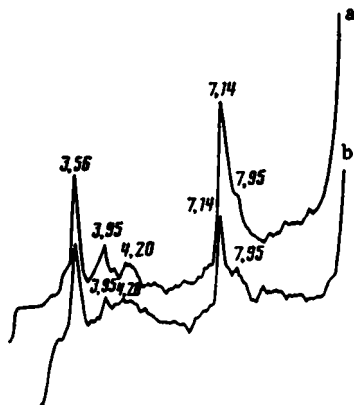


Fig. 4

Fig. 4. Diffractogram of the clay fraction of kaolinitic tonstein (sample 15): (a) natural; (b) glycerine-treated.

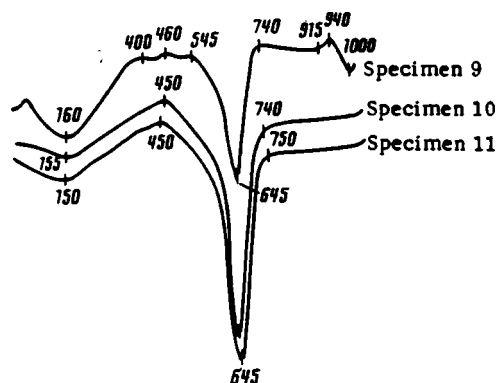


Fig. 5

Fig. 5. Heating curves of the clay fraction of kaolinitic tonsteins.

Impurity minerals include kaolinite with standard integral series of reflections 7.14 (001) and 3.56 kH (002) (Fig. 7, sample 35) and chlorite 7.0 (002) and 3.50 kH (004) (see Fig. 7, sample 37). Both samples contain illite, which produces the slight diffuse reflection 10 kH. A quantitative evaluation based on the intensity of basal reflections of the contents of clay minerals yielded the following values, %:

	Sample 35	Sample 37
Montmorillonite	70	90
Kaolinite	25	--
Chlorite	--	7
Illite	5	3

Distinct but weak reflections 7.95 and 3.95 kH indicate the presence of small amounts of heulandite.

Cheremkhovo tonsteins thus have a more complex mineral composition of the clay fraction; the individual interlayers are slightly different. No typical kaolinitic tonsteins have been determined here.

Thermograms reveal low-temperature endothermic effects at 170°C, typical for montmorillonite (Fig. 8). An exothermic peak at 530°C corresponds to ferruginous chlorite, presumably aphrosiderite; the endothermic effect at 630°C diagnoses kaolinite.

Chemical analyses (see Table 1) reveal a polycomponent composition of montmorillonitic tonsteins and are in agreement with a polymineral composition of the clay fraction. By the relationships of petrogenic components they are similar to montmorillonitic clays, in particular from Troshkov deposit [20]. The products of the Mesozoic crust of weathering on Siberian traps and volcanogenic rocks also have a similar composition [3]. The silicic modulus is higher (2.3-2.4) in montmorillonitic tonsteins with the presence of illite; it declines sharply (1.95) when the admixture is kaolinite.

Whether the montmorillonitic interlayers of Cheremkhovo deposit should be classified as tonsteins is an open question. Taking single mineral characteristics as the criterion, the submonomineral montmorillonitic interlayers in the coal seam of the Cheremkhovo deposit can be called tonsteins.

In completing the characterization of tonsteins, the morphology of the thickness of tonstein interlayers and their consistency should be described. The kaolinitic interlayers of the Azeisk deposit are more diverse in this respect. Three morphologic varieties of interlayers are distinguished: of a stable thickness, rosary-shaped, and intermittent. Interlayers of a steady thickness are well consistent over long distances regardless of the thickness. One such interlayer is traced over a stretch of up to 2 km with a practically constant thickness (5 cm) and clay mass composition. These interlayers have very sharp contacts with coal. Rosarylike interlayers appear as alternating bulges and constrictions which sometimes

TABLE 1. Chemical Compositions of Tonstein Samples from Irkutsk Basin, %

Component	Azeisk deposit					Cheremkhovo deposit		
	sample 6	sample 9	sample 10	sample 15	sample 27	sample 35	sample 36	sample 37
SiO ₂	43,31	32,29	46,18	44,96	44,42	50,13	53,75	53,78
Al ₂ O ₃	35,98	32,81	38,05	38,41	38,31	25,44	20,93	20,19
Fe ₂ O ₃ (gross)	0,42	0,45	0,27	0,71	1,95	4,24	4,45	2,60
CaO	0,41	5,20	0,28	0,37	0,43	1,26	1,42	1,42
BaO	0,02	1,09	0,02	0,02	0,01	0,04	0,03	0,03
MgO	0,16	0,11	0,12	0,22	0,24	1,88	3,07	3,36
MnO	0,02	0,02	0,01	0,01	0,01	0,01	0,02	0,01
TiO ₂	0,12	0,22	0,15	0,08	0,07	0,17	0,16	0,10
K ₂ O	0,13	0,11	0,17	0,15	0,15	1,21	1,33	1,29
Na ₂ O	<0,3	<0,3	<0,3	<0,3	<0,3	<0,3	<0,3	<0,3
P ₂ O ₅	0,03	7,38	0,03	0,06	0,02	0,01	0,02	0,01
Loss to heating	19,42	20,27	14,73	17,02	16,23	15,54	14,78	17,05
Sum	100,01	99,98	100,01	100,00	100,00	99,94	99,96	99,83
FeO	0,18	0,68	0,11	0,18	0,18	1,15	1,33	0,68
SiO ₂ /Al ₂ O ₃	1,20	0,98	1,19	1,40	1,10	1,95	2,31	2,40

become thin connections or wedge out on an interval. These interlayers are less consistent along the course; their composition, however, is fairly stable, although they include a noticeable coaly impurity. The thickness in the bulge portions attains 7 cm and in constrictions 2 cm.

The discontinuous interlayers are most complex and highly inconsistent. The kaolinitic matter in these interlayers is concentrated in thin strips, which alternate with equally thin coal strips or lines. Along the course, the kaolinitic strips wedge out; the interlayer is interrupted at that point in a combined wedging out; its continuation in the coal exhibits only small kaolinite insets. The contacts of these interlayers are blurred; they are up to 3 cm thick.

Thin (up to 3 cm) kaolinitic interlayers are more common; layers 5-10 cm thick are less frequent; one layer up to 20 cm thick has been described. Kaolinitic interlayers are fairly consistent along the course of the coal seams, but more variable and difficult to correlate with respect to the dip (see Fig. 1).

Montmorillonitic interlayers are thicker, consistent along the course, and free of coal admixtures.

SOURCES OF THE PARENT MATTER

Various theories have been advanced concerning the origins of the parent matter of tonsteins. Two alternative concepts treating tonsteins as derivatives of volcanic rocks or of sedimentary formations have some supportive evidence. Millot [12], after reviewing the pros and cons of the alternative theories, suggested that tonsteins may be of different origin. Burger and co-workers [22] shared this opinion, accepting both interpretations of their genesis.

Mineralogic and petrographic criteria are decisive in defining the parent material of a tonstein; in certain instances these criteria, however, may be inefficient when the "guiding" structures have disappeared. The origin of the parent material often is described hypothetically, based on intuitive conjectures, although there is a substantial volume of writing with reliable proofs of the source of the parent matter of these tonsteins.

Kaolinitic and montmorillonitic tonsteins of the deposits studied by us are in a favorable position; along with "faceless" interlayers, there are some with the clay mass containing relict textures or specific chemical features clearly indicating the source of clay matter.

Coarse-grained kaolinitic tonsteins provide informative genetic data. The nonuniform clay mass in them appears as an association of cryptocrystalline kaolinite and kaolinitic granules, with a characteristic silt-psammitic texture. Observations of the morphology of granules and their relationships with subcolloid kaolinitic mass of the cement show that coarse-grained kaolinitic tonsteins are terrigenous formations, while kaolinitic granules are clastogenic material. Many flint clays are known to have such a coarse-grained texture and are classified as clayey arenites [27]. In contrast to cryptocrystalline kaolinite in

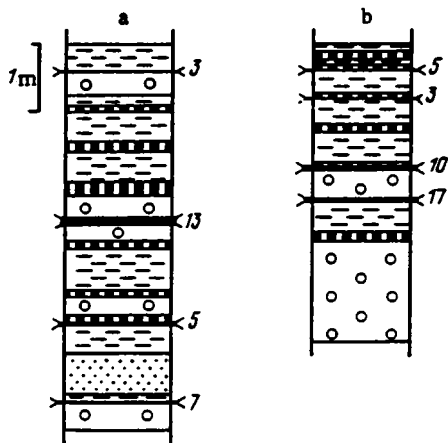


Fig. 6. Distribution of montmorillonitic tonstein interlayers in Glavnyi coal seam, Chermkhovo deposit. Notations as in Fig. 1.

cement, the kaolinite of granules exhibits crystallization; in different granules the structure is extremely homogeneous, pointing to a common source.

The large size of the granules and the different structural characteristics of kaolinite contradict a floccular genesis of the granules, although the flocculation mechanism of kaolinite sedimentation is known [25]. This theory could not explain the ideal differentiation of material, which brought nonclay minerals (quartz, feldspar, apatite, biotite, and zircon) into the subcolloidal kaolinitic mass, while keeping kaolinitic granules completely free of them. The different pigmentation of the kaolinite in the granules and the cement and the fact that mineral impurities are found only in the cement show that kaolinite was brought into the sedimentation basin with different degrees of dispersion. Assuming that the cement kaolinite pigmentation is primary and was acquired during the course of transportation and sedimentation, which is most probable, the colorless kaolinite of the granules would be representative of the parent rocks. This suggests that the material was brought into the interlayers already as kaolinite, i.e., that the latter is inherited. Kaolinite rocks were thus the source of tonstein material; their characteristics are identified from the texture of kaolinite in the granules. It is extremely homogeneous and does not differ from the texture of the kaolinites of the pre-Jurassic crust of weathering widespread in the basin [3, 17]. Coarse-grained kaolinitic tonsteins of the Azeisk deposit thus are terrigenous units; their clay matter was supplied by eroded kaolinitic crusts of weathering. The geologic and mineralogic-petrographic data available to us thus support the conventional hypothesis first enunciated by Pruvot [12] that tonsteins were formed from kaolinite brought into the coal accumulation basin from alimentation provinces. Zaritskii [5] proved a similar origin for tonsteins in the Donetsk Basin.

Cryptocrystalline kaolinitic tonsteins have isotropic or weakly polarizing clay mass with no relict textures. The parent matter of these tonsteins is thus often difficult to determine; it is only their association with coarse-grained kaolinitic tonsteins and similar associations of impurity minerals that indicates a common source — residual kaolinitic crust of weathering. Cryptocrystalline kaolinite is thus inherited, but, unlike kaolinitic granules, it is finely dispersed clay material of residual crust of weathering decayed by erosion.

The authors realize that the formation of submonomineral kaolinitic interlayers by mechanical transport of kaolinite may be perceived with doubt, as this mechanism requires peculiar environments. Such environments were conjectured by Keller [26], who believed that flint clays are indicators of potential sedimentary facies accumulating kaolinite. Short-lived existence of such facies does not seem to be exceptional, especially in periods of intense peat bog development; the formation of "sedimentary" kaolinitic tonsteins in such environments would be only dependent on the degree of development of crust of weathering in the supply area.

Montmorillonitic tonsteins consist of a homogeneous fine pelitomorph clay mass, sometimes with small kaolinite grains; the origin of the parent material can be judged only on the basis of chemical composition. A comparison of the contents of the principal petrogenic oxides of montmorillonitic tonsteins with the products of pre-Jurassic residual crusts of weathering reveals an important and remarkable feature: the chemistry of these tonsteins is quite similar to that of the products of crusts of weathering on traps. Since montmorillonitic

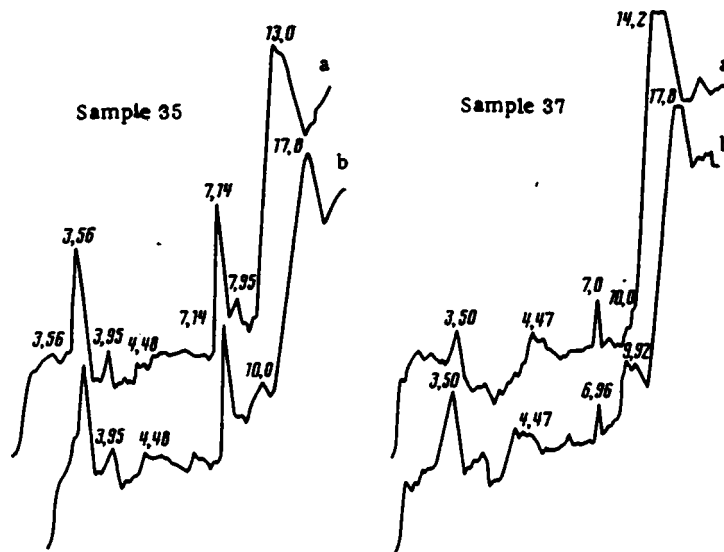


Fig. 7. Diffractograms of clay fractions of montmorillonitic tonsteins: (a) natural; (b) glycerine-treated.

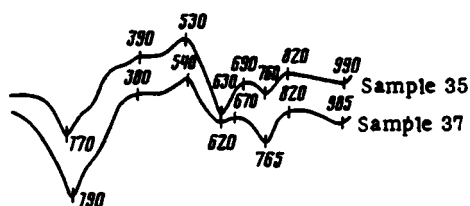


Fig. 8. Heating curves of the clay fraction of montmorillonitic tonsteins.

tonsteins are redeposited products of these crusts of weathering, the low contents of TiO_2 in the samples should not be surprising; these values, however, are higher than in kaolinitic tonsteins. For this reason, we believe that montmorillonitic tonsteins are also terrigenous formations, which received their clay matter from residual crusts of weathering on Siberian traps decayed by erosion. This peculiar source accounts for the submonomineral montmorillonitic composition of intercoal layers unusual for continental sediments: the primary stage of montmorillonitization requires the retention of Mg^{2+} , Ca^{2+} , Fe^{3+} , Na^+ , which is possible in a semiarid climate in the presence of ineffective lixiviation, and also in the presence of silicates, highly susceptible to hydrolysis, and having a specific surface, such as volcanic ash [26].

According to Weaver [15], who interpreted clay minerals as primary clastics reflecting the composition of the parent matter, montmorillonite can occur as the only clay mineral in a sediment, deposited in any conditions. An effective mechanism of segregation of clay mineral complexes, in his opinion, could be mechanical sorting.

Different mineral groups of tonsteins of the deposits of the Irkutsk Basin studied by us thus are products of redeposition of the corresponding crusts of weathering. This does not rule out, however, the presence in the basin of tonsteins formed by lixiviation of volcanogenic material in acid bogs, especially since the ash material of a rhyolitic composition has been recently found in the Jurassic of the Irkutsk depression [11]. As to the agents transporting clay matter, it is possible that a mechanical suspension of kaolinitic granules and a suspension of subcolloidal kaolinite was carried by slow streams; this hypothesis is supported by the close correlation of tonstein interlayers with members of banded coals and small oblique stratification of clay mass identified in individual interlayers.

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LITHOLOGY, FACIES AND HYDROCARBON CONTENT OF CALLOVIAN-KIMMERIDGIAN
DEPOSITS IN THE SALYM REGION OF WESTERN SIBERIA

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UDC 552.5:551.762(571.1)

The paper describes the lithology of the reservoirs and the enclosing rocks in detail. Exploration criteria are discussed along with genetic concepts of oil deposit formation.

Until recently, the Callovian-Kimmeridgian rocks of the Salym region and adjacent areas of the central Pre-Ob' area were not regarded as having oil potential. These deposits, as known [12] include significant amounts of clayey matter. The sandy facies of rocks of same age that include oil-bearing unit Yu, pinches out at a significant distance east and southeast of the Salym region (Fig. 1).

Industrial geophysical research data, partially also core information indicated the presence of carbonate lenses or intercalated strata in this sequence. However, a number of specialists treated these beds as septarian concentration horizons that by their nature did not produce open spaces between themselves. Therefore, they could not become reservoirs. Thus, these deposits were interpreted generally as regional mantle deposits. Furthermore, a number of papers associated with this mantle commercial petroleum resources of the Bazhenovsk Formation [6-11]. These publications suggested that impermeable facies of the Abalaks (cl-ox) and Georgievsk (km) formations only did prevent dispersion of carbon matter from the Bazhenovsk Formation oil source rocks, creating a highly productive petroleum-bearing unit.

Recent publications [1-4] have shown for the first time that permeable zones do exist in the upper portion of the Abalaks Formation. This was established during the general stratigraphic subdivision of the Bazhenovsk Formation and adjacent beds of Unit KS-1 (identification of Unit KS-1 by the author in 1981 was based on core analysis of drillholes #153-r and 135-r and on industrial geophysical information). It has also been shown that this unit contains a significant portion of the oil reserves that earlier has been attributed to the Bazhenovsk Formation. The presence of Unit KS-1 one has been demonstrated virtually everywhere in the Greater Salym deposits. Independent studies by the Siberian Scientific Research Institute (NII) of the Petroleum Industry (V. I. Belkin, E. P. Efremov, and N. D. Kaptelinin) and of the Yuganskneftegeofizika Trust (A. N. Zav'yalets, B. N. Zubarev, and V. P. Tolstolytkin) led to the uniform conclusion that the Unit KS-1 produces oil in 40% of the deposit area.

Information accumulated gradually to confirm the presence of commercial quantities of oil in Upper Jurassic deposits that underlie the Bazhenovsk Formation. Initially, this information was insufficient for a proper interpretation and for solving questions concerning reservoir lithology and genesis.

For this reason our disclosed data encountered fierce criticism on behalf of a number of workers, as the recognition of the role of the discussed units in the oil reservoir system in the Salym Region Upper Jurassic unavoidably led to reconsideration of the earlier accepted Bazhenovsk oil reservoir model. These geologists rejected even the possibility that significant effective reservoir capacity may exist in clayey unit J, beneath the Bazhenovsk Formation.

Others considered Unit KS-1 as a conduit through which oil migrated from the higher Bazhenovsk Formation, but which does not have inherent reservoir capacity.

The clashing options showed the need for a careful examination of data on the oil potential of Upper Jurassic deposits that underlie the Bazhenovsk Formation in the region. Such a review had been ordered in February, 1983 by the staff of the Minnefteprom of the USSR.

Siberian Scientific-Research Institute of the Petroleum Industry, Tyumen. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 99-111, May-June, 1987. Original article submitted July 23, 1985.

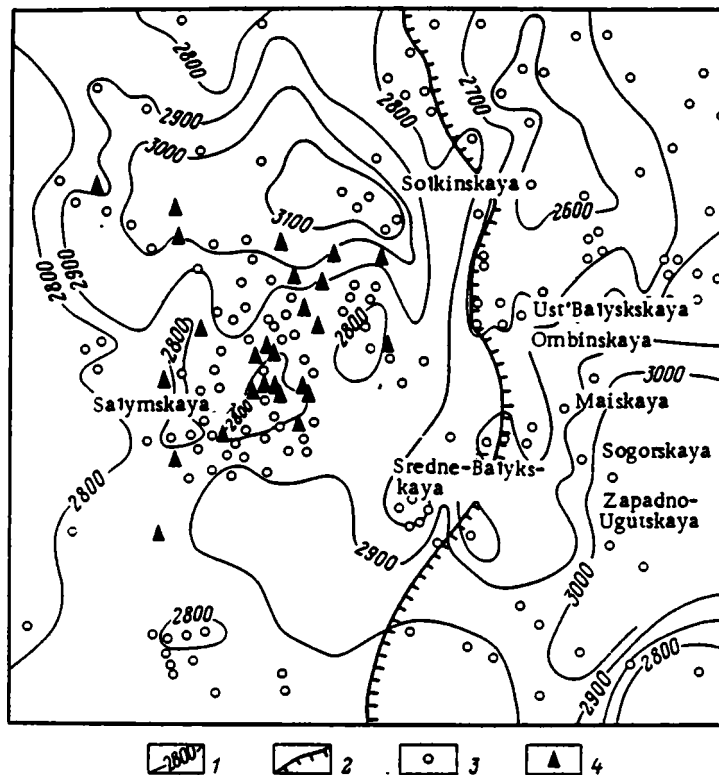


Fig. 1. Structural map of the Salym region and adjacent areas of the Surgutsk Arch along the crest of the productive bef KS-1(D₁). Structural contours of KS-1; 2) western boundary of the sandy facies of the Vasyugansk Horizon (boundary between the Vasyugansk and Abalask Formations); 3) drillholes that penetrated the section interval, discussed in the paper; 4) drillholes with commercial oil production from secondary reservoirs of Callovian-Kimmeridgian age. Exploration locations shown on map.

We have the first results of this review. Drillhole #554 in the Salym deposit obtained a full set of cores from the Bazhenovsk Formation and a large portion (15 m) of the underlying Callovian-Kimmeridgian sedimentary rocks. Core recovery (87.5%) was quite satisfactory. The Upper Jurassic interval in the drillhole has been subjected to differential hydrodynamic testing: formation testing, as formation penetration made it feasible tested individually two intervals of the Bazhenovsk Formation and one interval of the underlying deposits. The same section interval has been studied by a complex of geophysical drillhole investigations (GDI) that included geophysical control of the study (mechanical flow measurements, thermometry, thermoconductive method, density and moisture measurements).

Core studies of the Upper Jurassic rocks beneath the Bazhenovsk Formation in drillhole #554 identified five oil-saturated intervals (2750-2751.1; 2752.8-2754; 2755.6-2756.5; 2760.8-2761.0; 2762.3-2762.6 m). The three top ones were completely identified through drilling data; that included controlled well development. The lower productive zones of less oil-saturated occur directly by drillhole bottoms; they were essentially not shown by GIS logs. Mechanical flow meter data showed that the total oil discharge from the cited producing intervals in the Abalask Formation was 218 m³/day. The total initial production of drillhole #554 through a 1-cm-diameter flow regulator was 350 m³/day; from the Bazhenovsk Formation the yield was only a few tens of cubic meters per day. Data from drillhole #554 for the first time provided full documentation of large oil supplies in the underlying Bazhenovsk Formation within the producing strata (including Unit KS-1). Several geological, geophysical, and hydrodynamic methods were simultaneously employed; they provided results in mutual agreement. Drillhole #554 supplied the most complete set of data. However, among other drillholes, especially those, drilled between 1982-83 by the Salym UBR "Glavtyumenneftegaz" and being the most productive ones (drillholes #122, 123, 128, 135, 552, 559, 560, 565), according to GIS and

flow data, an interrelationship does exist between basic oil yield and the producing bed of the upper part of Callovian-Kimmeridgian stratigraphic horizon. According to L. Z. Pozin's (MINKhiGP) methodological handbook that deals with flow meter results of experimental-industrial exploitation of the Salym oil deposit by high-yield production wells, Unit KS is routinely penetrated in Upper Jurassic beds that underlie the Bazhenovsk Formation. Base flow (maximum 95%) was observed from this unit in drillholes #123, 559, 554, etc.

Previous denials of the high production potential of the "Sub-Bazhenovsk" portion of Upper Jurassic beds are thus deemed groundless. The presence of producing beds in this sequence can not be explained away by error or falsification of facts. We are dealing with a petroleum production target in the Salym deposit that earlier has been passed over. The following objections have been raised against this concept that, in the author's view, is entirely justified. An attempt was made by certain authors to include the uppermost Callovian-Kimmeridgian producing beds into the Bazhenovsk Formation; that is to change the boundary position between the Kimmeridgian and Volga Stages in the Salym region arbitrarily. This view interprets newly discovered productive beds as direct continuations of Callovian-Oxfordian sandy beds of the Vasyugansk Formation (Unit Yu₁) westward. These are known from adjacent areas of the Surgutsk Arch.

The first objection is very easy to refute. As shown earlier [1, 3, 4], the lower boundary of the Bazhenovsk Formation is almost always very sharp. The boundary is overlain by black, bituminous, hydrophobic (impervious) argillites and marls with rare, thin limestone beds; it is underlain by light greenish gray, water-saturated clays. Massive glauconite content caused the greenish coloration. Glauconite does not occur in the Bazhenovsk Formation but is most typical of the Kimmeridgian Georgievsk Formation [12]. All the lithological characteristics were also documented by the author in drillholes #135r, 153r, 120-bis; and 554. Directly below the discussed contact, drillhole #554 contained a *Meleagrinnella* cf. *subovalis* Mur fauna, representing Kimmeridgian at the youngest. A. I. Lebedev (ZapSibNIGNI) identified the fauna.

Finally, the industrial-geophysical characteristics of the contact are also very clearly defined, due to the sharp change in electric resistance of the interlayered water-saturated and water-repelling rocks. The induction method produced especially sharp contrasts.

Thus, the attempt to "drag" into the Bazhenovsk Formation the upper units of the underlying sequence, is absolutely unwarranted.

The second objection to identifying a new petroleum reservoir unit in the Upper Jurassic rocks is not quite acceptable, because Unit Yu₁ with which certain workers attempted to correlate Unit KS-1, and the other oil-bearing units of the "Sub-Bazhenovsk" Upper Jurassic deposits of the Salym region, are granular (sandy) reservoir units. Their age-correlatives are very unique clayey-siliceous-carbonate varieties. They belong to entirely different facies.

In order to stratigraphically correlate Unit KS-1 with other Callovian-Kimmeridgian productive units in the Salym region with Unit Yu₁, a detailed correlation has been accomplished between the Salym section and Upper Jurassic sections of Ust'-Balyksk, Srednebalysk, Maisk, Solkinsk, Sogorsk, Ombinsk, and the Western Ugutsk deposits of the Surgutsk Arch. It was shown that maximum 4-6 m thick the upper part of the "Sub-Bazhenovsk" section of the Salym region correlates perfectly with the Georgievsk Formation of the Surgutsk Arch lithologically and also based on industrial-geophysical data. Therefore, this formation is assigned to the upper part of the Kimmeridgian-Callovian rocks of the Salym region. The upper boundary of the Georgievsk Formation is drawn along the bottom of bituminous Bazhenovsk Formation rocks, the upper boundary along the top of the third (counting downward) producing Upper Jurassic unit beneath the Bazhenovsk Formation.

The Georgievsk Formation is of Kimmeridgian age, possibly also uppermost Oxfordian. In drillhole #554 2 m beneath the Georgievsk Formation, A. I. Lebedev identified *Cardioceras cordatum* and fragments of the ammonite *Cardioceras* sp. Thus, the Abalaks Formation sequence that, until now, has been thought to include the entire "Sub-Bazhenovsk" interval in the Salym region actually includes also the Kimmeridgian-Upper Oxfordian Georgievsk Formation. Lithologically, the Georgievsk Formation differs from the Abalaks in the lighter coloration of the rocks, mottling and a denser fracture network, accompanied by diagenetic slickenslide surfaces. In the more easterly parts of the Shirotnyi Pre-Ob' region, as in the Salym area, the Georgievsk Formation lithologically is identified and contrasted with the underlying Vasyugansk Formation by its clayey character, as opposed to the sandy character of the other formation. (However, the Vasyugansk Formation in the Sugutsk Arch area is mostly clayey, with

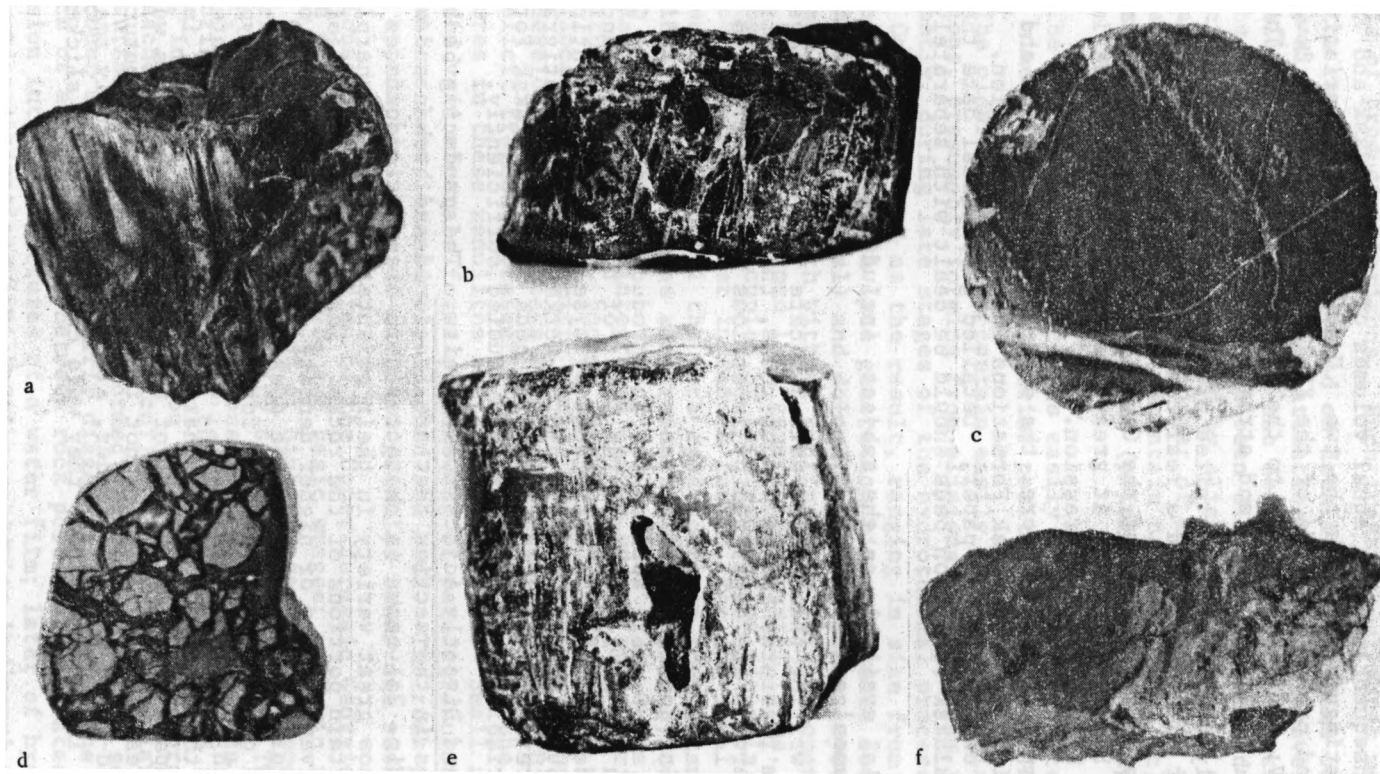


Fig. 2. Secondary reservoir rocks and the enclosing Callovian-Kimmerdgian rocks of the Shirot'naya Pre-Ob' Region. a) Clayey source rock of the producing bed of the Georgievsk Formation, with typical diagenetic slip surfaces, light-colored calcite encrustations locally on the fracture walls (drillhole #554; 2752.4-m depth); b) calcite and quartz veins along fractures in similar rocks. Quartz lighter colored. Microcavities in the vein centers (drillhole #57, 2874.2-m depth); c) fractures of different directions, mutually intersecting; white: crystalline quartz; dark: rhodochrosite; gray: calcite veins (drillhole #554, 2754.2-m depth); d) original rock that became completely disintegrated in the formation process of the vein minerals (limey argillite: light colored fragments in photograph); dark-colored vein formations (rhodochrosite and calcite); the upper part of the photo shows a twofold light-colored patch of a small cavity, polished surface; e) cavity in Layer D (drill-hole #153; 2935.0 m); f) "sprinkle" of quartz crystals on the cavity wall (drillhole #554; 2760.8-m depth).

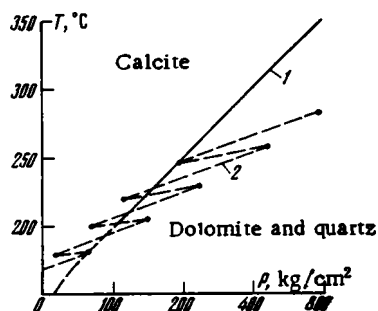


Fig. 3. Diagram of the evolution of hydrothermal process in reservoir rocks of the Upper Jurassic in the Salym region, under the impact of pulsating seismic stresses.

minor amounts of sandy units.) Consequently, when equal volumes of the Abalask and Vasyugansk Formations occur, it is easy to distinguish between the two. Unit Yu₁ and its variations belong to the Vasyugansk Formation and productive beds of the KS-1 unit and the next lower unit (Unit XIV—tentatively numbered by V. P. Tolstolytkin) to the Georgievsk Formation. Thus, Unit KS-1 can not be correlated with Yu₁ on lithological and stratigraphic grounds.

Unit Yu₁ may be correlated only with the lowest cited producing beds in the Upper Jurassic section of the Salym region. Their oil content and a real consistency are not known.

In contrast, the potentially productive beds of the Georgievsk Formation can be traced over a large area, not only in the Salym region but at great distances from it; over large areas of the Surgutsk Arch and the Khanti-Mansi Depression.

Our data reveal, much more completely than before, the structure, composition and genesis of the producing beds of the Georgievsk and Abalask Formations in the Salym region. This aspect of the problem is the topic of the present paper. Detailed geophysical data that confirm the presence of productive Abalask Formation beds should be dealt with separately in another paper by geophysicists.

The author uses all the material available on the subject, including data from the exploration drillhole drilled by "Glavtyumen'geologiya."

Stratigraphy. At the time of writing this paper, data indicate that the Georgievsk and Abalask Formation produce oil from fractures and cavernous rocks, that are a few centimeters to 2-3 m thick. The producing intervals are separated by impervious units, 1-1.5 m to 4-5 m thick.

The units were indexed according to the West Siberian system, as provided by ZapSibNIGNI [16]. Definitive index symbols G₁ and G₂ were applied for the producing units in the Georgievsk Formation, with provisional symbols for KS-1 and XIV. The first of these was given and maintained later by myself [1-4], the second was also introduced by myself and later continued to be used and temporarily reindexed by V. P. Tolstolytkin and co-workers [19]. Stratigraphic index symbols Ab₁, Ab₂, and Ab₃ were recommended for producing beds of the Abalask Formation. Their distribution and vertical variability has not yet been studied sufficiently.

Lithology of Reservoir Rocks and Directly Adjacent Rock Units. The producing beds are recurrent nonbituminous clayey rocks in the section that are fractured and broken and which occur in the area. Slickensides (Fig. 2a) occur on characteristic diagenetic surfaces in all fracture systems. The fractures show great variety in their orientation and are sharply curved. The fractures surround certain portions of the rocks. The structural-type joint fractures apparently form around given centers of higher density. Such joint systems often surround irregular-spherical, irregular-conical forms (the apex of the cone, upward in the section, reminds one of a miniature dome), or cylindrical forms (the so-called roll-type, with the cylinder axis parallel with the bedding surface). Sometimes, compaction centers are also visible; around which did the cited structural characteristics form. Thus, in drillhole #554 at 2761.5 m depth the compaction center of one of these roll-type features was a belemnite rostrum. In many instances such centers were not identified. These structural features were followed to the second-third magnitude order, along with increasingly smaller and more closely spaced fractures. In each instance, they were characterized by slickenside surfaces (Fig. 2b).

Similar rocks have been widely described as widespread from shallow water deposits of various ages from the Paleozoic to the Quaternary. Their characteristics and genesis have been discussed in an extensive literature [13, 14, 20, 21]. Such deposits are common in the

directly overlying rocks and even more common in rocks overlying coal beds in paralic coal basins. Sometimes they occupy the stratigraphic position of coal beds in such areas. Due to the very slow sediment accumulation and soil formation, they are very consistent areally over the large, level surface. Inside the associated producing beds, the discussed fractured clayey rocks are practically impermeable (in the industrial sense of the word), due to the density of the interior fractures and their "ground-in" nature along slickenside surfaces; also probably due to water-saturation of the ultrafine pore space. Traces of oil are non-existent in these fractures, even directly adjacent to contacts with oil-saturated carbonate cores.

Direct transition of the described fractured clayey rocks and producing carbonate varieties in drillhole #554 has been established. This supported the discussed conclusions on the genesis of producing horizons. Such transitional zones were only 10-15 cm thick.

The reservoir rocks (based on data from drillholes 554, 135, 120-bis, 135-r, 151-r and 153-r) display secondary carbonatization, including conversion into secondary marl. The partially silicified portion of the described clayey rocks resulted also from this process; all the gradual transitions have been directly documented in the cores. Fractures within producing layers are accompanied by slickenside surfaces and filled by few generations of vein minerals. Among these, in the order of mineralization: calcite, rhodochrosite, pyrite, dolomite and quartz (rock-crystal; mountain crystal) (Fig. 2c). Vein minerals, including the dominant, easily soluble varieties (primarily calcite) represent maximum 30-40% of the rock volume (Fig. 2d).

The paragenetic sequence was easily established; later generations intersect older ones, older minerals occupy more interior positions in the new mineral veins.

The older generations contain easily soluble minerals that precipitated from telethermal solutions, presumably forming from elisional waters from the overlying Bazhenovsk Formation. Apparently, during late stages of the hydrothermal process part of the minerals was leached out. Cavities formed as the result, ranging in size from fractions of a millimeter to 2-3 cm (Fig. 2e). Telethermal late generation mineral druses formed on the walls of large cavities: quartz (mountain crystal) and dolomite. The perfect crystal habits of these newly formed minerals indicate growth without confinement. Often, open spaces, as large as 1-2 cm or more, occur between newly formed late generation crystal forms. In other instances, all open spaces have been completely occupied by late generation minerals. Deeply corroded, friable disintegration products in other instances formed from the total vein mineral mass. Small, brittle fragments formed and all the pore space between them became oil-filled, as were the large cavities. These fragment surfaces often are covered by quartz crystal "bristles" (Fig. 2f).

Relicts of the disintegrated clayey source rocks, originally containing the described oil-saturated intervals, became impregnated by carbonate cement and thus turned into secondary marl (locally, into dolomitic marl). Less frequently, the rock became silicified. During the vein development these rocks became much denser and in this process they started to spall. The relict fragments presently occur as xenoliths in the rock, composed of vein minerals. Fractures in these xenoliths are also oil-filled. Small xenolith fragments and remnants of corroded vein minerals forms a framework of pseudogranular reservoir rock when strongly corrosive waters have intensively leached the rock. The rock permeability and flow-through capacity (FES) approached those of the best granular reservoir rocks.

Consequently, formation of the Upper Jurassic Georgievsk-Abalask interval in the Salym region may be subdivided into two basic stages; each, in turn, into two substages. The first stage concludes with formation of highly heterogeneous rocks. Initially, a detrital-gravelly weathering zone, or corresponding soil profile formed. The abundance of reactive organic matter, as under similar conditions in soils of coal beds, hindered development of a weathering horizon or (more exactly) of the soil profile beyond this initial stage. Only at a higher level, in the Georgievsk Formation did these processes progress somewhat farther, as indicated by bleached colors (grey formation?) and significantly large number of fractures with slickenside surfaces. Such surfaces formed already during the second stage of reservoir formation, on account of its initial (early diagenetic) burial. The slickenside surfaces resulted in the absence of any connection between rock portions, separated by fractures. This facilitated the intrusion into the fractures of a water film; later of hydrothermal solutions. The presence of numerous generations indicate the pulsating character of the hydrothermal process. The following patterns had been noted:

Mobilization of compounds that produced minerals of earlier generations, such as calcite, required increased pressure (total pressure that may exceed lithostatic pressure) or lowered temperatures. Precipitation of the cited minerals would require increased temperatures or decrease in pressure. For mobilization and subsequent precipitation of SiO_2 from the solution opposite conditions would be required. This easily explains the areal separation between quartz and calcite mineralization, the presence of quartz on cavity walls that form as the result of calcite leaching. An explanation is hard to come by for the frequent temperature fluctuations. Pressure fluctuations are much easier to explain, especially in seismically active zones. As known [23], pressure fluctuations in earthquake danger zones occurred hundreds and even thousands of times during historic times. It may be assumed that ten or more such pulses occurred in seismically active (though not danger zones), along mobile boundaries between tectonic blocks, during the time between sediment accumulation and the filling of reservoir rocks with petroleum within these sediments. These events may have taken place approximately during the Middle Paleogene. This assumption would explain the linear arrangement of productive zones in the Upper Jurassic Salym area deposits [22], their association with the zone of disjunct dislocations (the boundary between tectonic block); first demonstrated by I. I. Bobrovnik as early as 1979.

The final stages of oil deposit formation (oil saturation of reservoir) generally preceded late mineralization (quartz and dolomite). This is shown by the quartz and dolomite crystal cover on the cavity walls and observations by Yu. V. Shchepetkin of ZapSibNIGNI (pers. comm.) on liquid inclusions of oil in the discussed quartz crystals. Apparently, supersaturated silica solutions migrated through the cavity systems in the units in question and deposited quartz crystals on the cavity walls during corresponding PT-changes. These solutions already included finely dispersed liquid oil. Quartz and dolomite form a stable association while lowering the temperature at stable pressure, or when raising pressure while keeping temperature at the same level. Pulsating changes in the pressures in seismically active zones lead to relatively faster increase in pressure than of temperature in the compression phase, and correspondingly, to slower changes in the temperature than of pressure in the dilation phase (Fig. 3). The pulsating pressure-temperature changes are shown in this diagram through the stability field of quartz and of the dolomite + quartz association as quoted in Bulakh [5]. Analysis of the curves (Fig. 3) indicated the mineralization sequence of various vein minerals in the above-discussed rocks. Each cycle of increased seismic pressures was accompanied by (against a background of regional increases in P and T values) impulse growth in the T (moderate) and P (faster) values. This inevitably moves the system into the field of greater quartz and dolomite stability.

If one accepts the theory of a Bazhenovsk Formation origin of at least of part of the oil and that this oil fills the described traps, the abundance of dolomite in the late generations of the described vein minerals agrees well with the assumptions that relate to oil forming processes in the overlying Bazhenovsk Formation. The carbonaceous matter becomes desorbed during montmorillonite illitization (the connection between these processes has been established by Zkhuz [11]). Illitization of montmorillonite must be accompanied by massive Mg-ion separation, easily substituted by Ca ions, during rising pressures. As the reservoir becomes oil-filled, the hydrothermal process would inevitably stop.

The discussed producing intervals of the Georgivsk and Abalask Formations are shown by industrial geophysical (electric log) data to be high resistivity zones. Radiometric logging has shown high gamma activity and lower hydrogen content. Acoustic logs displayed sharply fluctuating values of acoustic impedance. They are very clearly displayed by the ρ_k -peaks of the B-logs, against a background of quite low electric resistivity clayey rocks that include the basis nonproducing portions of the Callovian-Kimmeridgian sequence.

Lithology of Rocks That Separate Producing Units. We have already touched on the composition of rocks in the intervals that directly include productive carbonatized beds. At some distance from the beds that include the discussed reservoir rocks, the diagenetic slickenside surfaces become very rare or disappear altogether. The rocks there are gray, nonbituminous and hydrophyllic clayey varieties, less lithified and more plastic on the average than the overlying Bazhenovsk Formation argillites. In contrast with these, certain varieties of the Abalask and, especially the Georgievsk clayey rocks may be called consolidated argillite-like clays. These rocks usually are very finely dispersed types, with faunal and plant detritus fragments that often are pyritized. Thin-walled and well-preserved bivalve shells predominate in the fossil fauna. In contrast with the overlying Bazhenovsk Formation, the fossils contain almost no *Inoceramus* and *Buchia*, but many pectinides (*Meleagrinea*). Some-

what rarer are ammonite impressions and belemnite rostra. The plant fragments often include stems and fusinized fragments of woody land plants and also numerous rootlets of land plants that became buried in life positions, perpendicular to sediment layering. These indicate the very shallow facies of the deposits. Pyritized, jarositized plant fragments are very common, sideritized plant detritus less frequent. These are common in very shallow facies with slow sediment accumulation rates; in transgressive or "backwater" facies. Shallow water indications increase upward in the Abalaksk Formation sequence. In the Georgievsk Formation clayey rock covers carry surficial indications of weathering and soil formation; they are strongly bleached, mottled, with common hypergenetic spherulite and pisolith formations. Mottling sometimes is the result of kaolinite mineralization. A clear interpretation of the hypergenetic mineralization in the Georgievsk Formation was complicated by the fact that the subsequent Bazhenovsk transgression and catagenesis severely altered these minerals. In addition, processes of weathering crust formation over sedimentary rocks that originally certainly occurred in the Georgievsk Formation made it difficult to introduce these rocks unaltered into the weathering horizon.

The shallow water depositional character of the sediments and the great likelihood that they were involved in the hypergenetic zone were not contradicted by the massive presence of glauconite in the Georgievsk Formation and its absence in the overlying Bazhenovsk Formation. A huge literature deals with the genetic problems of glauconite. Nalivkin [17] cites three groups of genetic theories. Glauconites occur also in shallow marine and continental basin deposits. They also form during catagenesis of carbonates [15]. The mineral is only absent from deep water sediments, as indicated at the end of the last century by J. Murray and A. F. Renard.

The Georgievsk clays are the most water-saturated rocks within the Upper Jurassic section of the Salym region. The cover units of the Georgievsk and Abalaksk Formations are very widespread in their areal distribution. Thus, no drillholes are known in the Greater Salym deposits that totally penetrate this interval and which did not encounter the highest unit in this sequence, represented by clays of given sorting characteristics. It belongs to stratigraphic unit KS-2.

Oil Content of the Georgievsk and Abalaksk Formations. Earlier we provided data on the relative role of the Georgievsk-Abalaksk interval in the total oil content of the Upper Jurassic in the Salym region. In evaluating them, one must take into account that the overwhelming majority of the exploration and production wells in the Salym deposit reached only the top of the Georgievsk Formation and only occasionally did they penetrate its highest producing horizon KS-1. Only in relatively rare instances did the wells penetrate the second producing horizon of this formation. The producing units of the Abalaksk Formation have been drilled but in a few drillholes; their detailed description and stratigraphic identification has been made only in drillhole #554 and even that penetrated only portion of the Abalaksk Formation. Of the more than 300 drillholes drilled in the area of the deposit, the Callovian-Kimmeridgian interval has been penetrated completely only in 18. Therefore, present data on the productivity of the Georgievsk and Abalaksk Formations is very incomplete, due to unfavorable conditions of the sampling and subsequent research work on the Georgievsk producing units. In most instances the producing beds in the Georgievsk Formation (mostly unit KS-1) have been penetrated near the well bottoms, virtually at their sump. This occasionally has contaminated the drill-penetrated producing interval in the Formation. This to a great extent, resulted from exchange of matter through solutions in drilling muds. Thus, out of 59 producing drillholes, drilled by the beginning of 1983, unit KS-1 was penetrated in 50 wells. Out of these, in 22 drillholes the borehole bottoms were above the top of the Georgievsk Formation. Increased contamination of the Georgievsk-Abalaksk drillhole intervals probably is partially explainable also by the significant oil flux through the drillpipe from the Bazhenovsk Formation into unit KS-1. This was repeatedly found when penetrating this part of the section. These oil fluxes were caused by significant high initial formation pressures in the Bazhenovsk Formation, in contrast with those in the Abalaksk Formation. The producing units in the Bazhenovsk Formation typically have anomalous high formation pressures (AHFP), with an anomaly index of 1.6-1.7. Still very sketchy data indicate that the initial formation pressures in unit KS-1 and probably in the other producing units of the Abalaksk Formation exceed hydrostatic pressures by more than 20-30%.

Thus, current information on the oil content of the Georgievsk and Abalaksk Formation is sufficiently not only because the Abalaksk Formation has been incompletely penetrated in but a few drillholes, but also due to technological conditions of penetration, if only in the highest producing beds.

For this reason we are aware of the fact that the study of oil content in the Georgievsk and Abalaksk formations in the Salym and adjacent regions of western Siberia is still in its initial phase and calculations of the oil extraction potential in the present paper would be premature. This indisputable fact is complicated by the very close proximity of the producing units in the Georgievsk, Abalaksk, and Bazhenovsk formations. Their joint testing would exaggerate the yield from the Bazhenovsk formation at the expense of yield from the underlying rocks. The scale of this exaggeration is indicated by the following: 48 wells produced a maximum of over 100 m³/day; only one of them (#78-r) did not produce from Unit KS-1. The other wells, based on the production history of wells, gas log results and composition of drill mud, brought up with the oil, indicated production either only from the Georgievsk-Abalaksk interval (mostly from Unit KS-1, as most drillholes did not penetrate deeper), or among them to that interval, while the inflow from below — according to all data — played a significant role. Of the 19 instances of spontaneous gushing when Upper Jurassic sedimentary rocks were drilled in the Salym region, 14 were related to drilling into the Georgievsk formation. This clearly establishes connection between record oil flow from drillholes #141 and 129, with over 1000 m³/day production, and the "Sub-Bazhenovsk" interval of the section. Without exceptions, when production was increased in production tests (OPÉ), the measures employed were those that were aimed at increasing oil yield from Unit KS-1 (flushing and cleaning of well bottoms, acid treatment, etc.).

It follows, that the still incompletely explored oil-bearing rocks of the Georgievsk-Abalaksk interval represent oil prospects. The interval is at least comparable with the Bazhenovsk formation in this respect, but may surpass it in its potential.

The high oil-saturation of the Georgievsk-Abalaksk rocks may partially be explained by their better sorting. While oil in the Bazhenovsk reservoir may appear in a "smeared" state in the microfractures and ultra-fine pores of the hydrophobic clayey "matrix" that represents more than half the Bazhenovsk Formation volume in the Salym region, oil in the Georgievsk and Abalaksk reservoir rocks, due to sealing by the practically impermeable cover units, were not expelled at all from these rocks. The cover rocks are composed of hydrophilic and water-saturated, relatively plastic clays.

In addition, the volume, the hydraulic factor (ϕ), and the porosity in the reservoir rocks of the Georgievsk-Abalaksk apparently are of significantly higher values than in the Bazhenovsk formation.

* * *

In summary, the newly penetrated reservoirs and the enclosed oil deposits of the Callovian-Kimmeridgian interval had very similar formation conditions to those of the hydrothermal ore deposits. The difference lies in the fact that instead of solid ore precipitate, fluid organic matter occupies the pore space that formed during hydrothermal processes. This fluid is the last "sublimate" and completes a process of mineral resource formation. This process in all likelihood has been greatly facilitated by the proximity between the studied beds and petroleum source rocks of the Bazhenovsk Formation. Another factor that led to the formation of the deposit: an association with a seismically stressed zone and related boundaries of, apparently, to tectonic blocks that are well manifested in friable rocks of the folded basement and slightly replaced in the plastic sedimentary cover. In the last stage of tectonic (seismic) activity, particularly of disjunct nature, unmarked by dislocations, such activity was marked only by stress (pressure) fluctuations. The third factor was characterized by the presence of hypergenetic rock alterations (a detrital weathering zone or soil profile). Rock expansion took place in those areas in which beds of these rocks crossed seismically stressed zones, in conjunction with hydrothermal processes that led to reservoir formation and collection of oil in these reservoirs. The hydrothermal process leads to the formation and permanent documentation of results of hydraulic autoerosion. This erosive process was suggested [10, 18] as being the main factor in reservoir formation in Bazhenovsk-type reservoirs. However, it was not taken into account that in the establishment of pore spaces that form during hydrothermal activity a skeletal framework is required. Otherwise, the pore space would close up again and the fluid expelled from it. Vein minerals, due to partial leaching, form just this kind of framework.

Thus, certain research criteria have been established in newly explored Sub-Bazhenovsk oil deposits of the Salym type. These are most timely as they form the basis for assuming the presence of similar deposits in a number of areas adjacent to the Salym deposits (e.g.,

the Pravdinsk deposits). Discovery of such deposits may be accomplished when conditions, similar to those discussed in the present paper are found. This may be a significant contribution to the national economy.

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DISTRIBUTION OF GOLD AND CARBON IN TERRIGENOUS DEPOSITS
OF CENTRAL KOLYMA AND THE LOCALIZATION OF GOLD MINERALIZATION

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UDC 553.411.071(571.5)

It is shown that carbonaceous material dispersed through terrigenous deposits forms a geochemical barrier promoting the precipitation of gold from hydro-thermal solutions.

The role of primary concentrations of gold and carbon in localizing gold mineralization in terrigenous deposits, which generally form the upper levels of miogeosynclinal basins, has been studied chiefly in areas when the deposits are of Precambrian to Paleozoic age and have been metamorphosed to the greenschist facies. Terrigenous deposits of the Verkhoyansk complex (Upper Permian-Jurassic) in the southeastern part of the Yano-Kolyma foldbelt are Mesozoic, and overlie carbonate beds and carbonaceous deposits of presumed Lower and Middle Paleozoic age.

The most characteristic features of the foldbelt include the following: linear extent with broad, relatively simple folds; relatively uniform terrigenous composition with minor pyroclastics in some parts of the section; weak regional metamorphism which does not reach the greenschist facies; widespread granitoid intrusions and dikes of different ages, which vary in size and structural position.

Despite the relatively young age of the terrigenous deposits, the geologic setting of the gold ore has much in common with localizing conditions of older foldbelt gold deposits: the same kind of miogeosynclinal basin filled with terrigenous deposits more than 10 km thick, a similar content of organic matter, and the same morphological types of ore mineralization (from disseminated to vein); simplicity of mineral associations (mainly pyrite-arsenopyrite); paragenetic association of mineralization with dikes and small intrusions; widespread metasomatism and the importance of carbon in localizing mineralization.

The southeastern part of the Yano-Kolyma foldbelt is divided by a major northwest-trending fault into two main structural elements: the In'yali-Debinsk megasynclinalorium, composing the more interior, downwarped part of the folded area and containing Mesozoic rocks, and the Ayan-Yuryakh anticlinorium, the outer, upwarped part of the area with exposures of Upper Permian rocks. These structural elements are considered to be a structural-metallogenic zone characterized by gold content.

Lithologic and stratigraphic factors controlling gold mineralization have previously been given much attention. For example, Firsov [4] noted that the source of mineralization was sedimentary rocks involved in profound regional metamorphism, as a result of which gold migrated to upper levels of the sedimentary complex. According to Serebryakov [2], Ol'shevskii [1], and other investigators, gold ore is restricted to stratigraphic units of the Vekhoysansk complex which are distinguished by an increased concentration of carbonaceous material and, presumably, gold. The problem with these papers is their lack of analyses of gold and organic matter content in the host rock of the ore deposits, which makes it impossible to resolve the question of the presence of significant primary sedimentary gold which could serve as a source of the ore.

In order to fill this gap, we ran three geological-geochemical profiles across the trend of the structure and metallogenic zone: two in the In'yali-Debinsk zone and one in the Ayan-Yuryakh zone, including typical gold-bearing areas. Samples of unaltered sedimentary rock, mainly from outcrop, were taken along these profiles. Prepared samples were analyzed in the laboratories of TsNIGRI, the Central Scientific Research and Exploration Institute for Nonferrous, Rare, and Noble Metals for their gold content using spectrochemical methods and for their organic matter content using chemical methods.

Central Scientific Research and Exploration Institute for Nonferrous, Rare, and Noble Metals, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 112-118, May-June, 1987. Original article submitted November 5, 1985.

The Verkhoyansk complex consists of interbedded siltstones, mudstones, sandstones with sparse beds of tuffaceous rock, and conglomerates. The sandstones are dense, massive, gray to light gray, indistinctly bedded or locally evenly bedded, and are polymictic or oligomictic in composition. They are composed of angular, rarely rounded, sometimes weakly corroded fragments of quartz, plagioclase, and potassium feldspar, and scattered fragments of mudstone, volcanic glass, andesites, carbonates, and flakes of muscovite. The cement is porosity type, locally contact, rarely basal, and in composition siliceous-clay, sericite-clay, sometimes carbonate. The ore minerals are pyrite with accessory apatite, zircon, tourmaline, and leucosene. Secondary minerals include sericite, carbonates, and chlorite, and are developed in minor amounts in the cement. Siltstones are distinguished from sandstones by their dark color. Clearly expressed bedding and sometimes crossbedding, and finer grain size. The mudstones are usually black with a platy, fissile, or rarely massive structure, and are lenticular to irregularly bedded. They are composed of sericitic-clayey material with a considerable amount of organic matter. They are pelitic, locally silty, in texture. Tuffaceous rocks, mainly tuffaceous siltstones, are distinguished by a significant content of pyroclastic material: fragments of volcanic glass, andesite, and crystals of plagioclase, potassium feldspar, and quartz. Conglomerates are generally located at the base of suites or sequences, marking intraformational unconformities. The pebbles are medium to well rounded fragments of sandstone, siltstone, mudstone, and quartz, and the cement is sandy-clayey.

Study of the gold content of the terrigenous section of the Verkhoyansk complex has shown that gold generally amounts to 5.3 mg/ton in central Kolyma. This amount can be taken as the local clark of concentration (Tables 1-3). The average content in rocks of the various metallogenic zones is quite similar: 5.2 mg/ton in In'yali-Debinsk and 6.2 mg/ton in Ayan-Yuryakh, which markedly exceeds the clark for terrigenous rocks.

The overall distribution of gold in the terrigenous complex follows a lognormal law with a unimodal orthosymmetrical curve of content and an excess in the range 2-4 mg/ton. Histograms of the gold content in siltstones and mudstones are lognormal or close to normal with considerable dispersion. Sandstones are distinguished by a lower dispersion of content and very irregular distribution of the gold. The gold content decreases somewhat in the direction of younger rocks. Thus, it averages 6 mg/ton in Upper Permian to Triassic beds, 5.9 mg/ton in Lower Jurassic, and up to 4.9 mg/ton in Middle Jurassic strata.

The increased gold content in pyritic sediments should be noted. Pyrite is found in three forms. The first, probably the earliest, consists of fine irregularly shaped grains, nodules, and lenses. The second includes cubic crystals 1-2 mm to as much as 5-10 mm in size, mainly present at lithologic contacts or in siltstone and sandstone interbeds in mudstone. Spiky borders of quartz are sometimes developed around the pyrite crystals. The third form of pyrite is found in phosphorite concretions, in which large (1-10 mm) crystals of pyrite of the third form are arranged concentrically with randomly oriented fine crystals of pyrite of the second form. The concretions apparently formed during diagenesis of the sediments, as indicated by the stratification of the concretion-bearing bed, which is preserved in the concretion, and by the presence of randomly oriented pyrite outside of the concretions.

Isotopic studies of the sulfur show that pyrite in terrigenous beds, according to 18 analyses, is characterized by a considerable scatter in $\delta^{34}\text{S}$ values from +17.8 to -15.69%, with predominance of pyrite enriched in the light isotope of sulfur. This suggests that biogenic sulfur in sediments took part in the formation of pyrite. A more stable ratio between light and heavy isotopes of sulfur was found in sulfides in the gold ore.

From the above it follows that the origin and time of formation of diagenetic pyrite in terrigenous sediments differed from that of gold mineralization. This difference is also reflected in the trace element composition on the sulfides: an increased concentration of arsenic, gold, silver, nickel, and cobalt and a decrease in copper and lead are found locally in sulfide deposits. At the same time, the geochemical features of diagenetic pyrite in terrigenous rocks in the gold ore areas and outside of them are quite similar.

Diagenetic pyrite is no doubt a concentrator of primary sedimentary gold, but the pyrite content in terrigenous rocks usually does not exceed a few percent and therefore does not have a significant effect on the gold content. On the other hand, granitoid intrusions in the Kolyma and other complexes, assimilating rocks of the Verkhoyansk complex, mobilize quantities of gold, which considerably improves the ore-generating potential of the intrusions.

The distribution of carbonaceous matter (CM) in rocks of the Verkhoyansk complex, according to analytic data from the samples analyzed for gold, is presented in Tables 1-3. It

TABLE 1. Au and C_{org} in Terrigenous Rocks of the Ayan-Yuryakh Anticlinorium (profile 1)

System	Sequence, suite	Sandstone		Siltstone		Siltstone		Mudstone	
		Au, mg/ton	C _{org} , %	Au, mg/ton	C _{org} , %	Au, mg/ton	C _{org} , %	Au, mg/ton	C _{org} , %
Triassic	Upper	—	—	$\frac{9,5 (5)}{3,0-17,0}$	$\frac{0,48 (5)}{0,31-0,66}$	—	—	—	—
	Lower	—	—	$\frac{7,7 (10)}{2,6-15}$	$\frac{0,53 (10)}{0,25-0,91}$	—	—	3,0 (1)	0,75 (1)
Permian	Kulinsk	—	—	$\frac{7,2 (10)}{3-8,6}$	$\frac{0,57 (10)}{0,27-0,78}$	—	—	$\frac{5,1 (3)}{3,3-6,5}$	$\frac{0,8 (3)}{0,36-1,65}$
	Neryuchinsk	4,4 (1)	0,22 (1)	$\frac{6,0 (4)}{4-11}$	$\frac{0,69 (4)}{0,55-0,82}$	$\frac{4,8 (8)}{2,5-8}$	$\frac{0,6 (8)}{0,22-1,01}$	$\frac{4,3 (2)}{4,2-4,4}$	$\frac{1,1 (2)}{0,96-1,24}$
	Atkans	$\frac{6,1 (6)}{3-9}$	$\frac{0,13 (6)}{0,1-0,22}$	—	—	$\frac{4,2 (12)}{2-7,4}$	$\frac{0,27 (14)}{0,1-0,4}$	$\frac{5,2 (5)}{3,3-6,8}$	$\frac{0,86 (5)}{0,29-1,13}$
	Tassk	$\frac{6,8 (3)}{5,3-8,7}$	$\frac{0,2 (3)}{0,1-0,37}$	$\frac{8,0 (12)}{3,6-11}$	$\frac{1,27 (12)}{0,14-1,9}$	$\frac{2,5 (2)}{2,5-2,6}$	$\frac{0,33 (3)}{0,22-0,4}$	$\frac{5,4 (7)}{2,5-14}$	$\frac{1,52 (7)}{0,72-2,46}$

Note: in this and the following tables the numerator is average content, the denominator is the range, and the number of samples is in parentheses.

TABLE 2. Au and C_{org} Content in Terrigenous Rocks of the In'yali-Debinsk Synclinorium (profile 2)

System	Series	Sequence	Sandstone		Siltstone		Mudstone		Pyritized rocks	
			Au, mg/ton	C _{org} , %	Au, mg/ton	C _{org} , %	Au, mg/ton	C _{org} , %	Au, mg/ton	C _{org} , %
Jurassic	Middle	Upper	$\frac{3,9 (11)}{2-7,4}$	$\frac{0,19 (11)}{0,07-0,75}$	$\frac{4,0 (67)}{2-10}$	$\frac{0,18 (67)}{0,09-0,71}$	$\frac{5,0 (37)}{2-39}$	$\frac{0,63 (37)}{0,19-1,21}$	$\frac{3,3 (12)}{2-6,3}$	$\frac{0,2 (12)}{0,12-0,34}$
		Lower	$\frac{5,9 (19)}{2-17}$	$\frac{0,2 (19)}{0,05-0,44}$	$\frac{5,1 (89)}{2-21}$	$\frac{0,21 (89)}{0,1-0,66}$	$\frac{4,4 (64)}{2-18}$	$\frac{0,46 (64)}{0,24-1,21}$	$\frac{5,6 (8)}{2-17}$	$\frac{0,18 (8)}{0,05-0,25}$
	Lower	Upper	$\frac{7,7 (14)}{2-13}$	$\frac{0,14 (14)}{0,03-0,28}$	$\frac{5,5 (63)}{2-19}$	$\frac{0,2 (63)}{0,1-0,64}$	$\frac{6,6 (32)}{2-28}$	$\frac{0,44 (32)}{0,13-0,9}$	$\frac{5,8 (7)}{3-15}$	$\frac{0,28 (7)}{0,24-0,5}$
		Lower	—	—	$\frac{3,8 (8)}{2-10}$	$\frac{0,13 (8)}{0,06-0,25}$	$\frac{4,6 (7)}{3-9}$	$\frac{0,51 (7)}{0,32-0,96}$	$\frac{3,9 (2)}{2,7-5}$	$\frac{0,26 (2)}{0,25-0,28}$

TABLE 3. Au and Corg Content in Terrigenous Rocks of the In'yali-Debinsk Synclinorium (profile 3)

System	Series, suite	Conglomerate		Sandstone		Siltstone		Tuffaceous siltstone		Mudstone	
		Au, mg/ton	C _{org.} %	Au, mg/ton	C _{org.} %	Au, mg/ton	C _{org.} %	Au, mg/ton	C _{org.} %	Au, mg/ton	C _{org.} %
Jurassic	Zhukov	—	—	$\frac{7,0 (2)}{4-10}$	$\frac{0,19 (2)}{0,14-0,25}$	$\frac{9,1 (4)}{6,9-10}$	$\frac{0,47 (4)}{0,29-0,81}$	—	—	$\frac{6,0 (6)}{2,5-12}$	$\frac{1,08 (6)}{0,44-1,65}$
	Myaundzhinsk	—	—	$\frac{5,8 (15)}{2-11}$	$\frac{0,19 (15)}{0,09-0,43}$	$\frac{6,3 (29)}{2-16}$	$\frac{0,37 (29)}{0,11-1,84}$	17,0 (1)	0,58 (1)	$\frac{5,5 (19)}{2,2-14}$	$\frac{0,9 (19)}{0,48-1,55}$
	Kadykchansk	$\frac{2,7 (4)}{2-3,8}$	$\frac{0,12 (4)}{0,07-0,15}$	10,0 (1)	0,24 (1)	$\frac{5,0 (3)}{2-8,3}$	$\frac{0,24 (3)}{0,13-0,43}$	$\frac{3,7 (5)}{2-7,3}$	$\frac{0,5 (5)}{0,34-0,93}$	$\frac{6,4 (4)}{2,8-9,3}$	$\frac{0,47 (4)}{0,24-0,68}$
Triassic	Lower, undifferentiated	—	—	$\frac{4,7 (15)}{2-18}$	$\frac{0,14 (15)}{0,08-0,28}$	$\frac{6,7 (29)}{2-18}$	$\frac{0,42 (29)}{0,11-1,86}$	—	—	$\frac{6,2 (27)}{2-17}$	$\frac{0,83 (27)}{0,31-2,1}$
	Upper	—	—	9,6 (1)	0,09 (1)	—	—	—	—	4,3 (1)	0,29 (1)
	Middle	$\frac{12,0 (3)}{2-30}$	$\frac{0,17 (3)}{0,08-0,29}$	$\frac{4,6 (3)}{3-7,3}$	$\frac{0,1 (3)}{0,06-0,14}$	$\frac{4,1 (9)}{2-6,8}$	$\frac{0,48 (9)}{0,35-0,77}$	—	—	$\frac{5,5 (4)}{4,6-6,2}$	$\frac{1,08 (3)}{0,63-1,4}$

can be seen from these data that the average CM content for the whole region is 0.42%. This value ranges from 0.33 to 0.45% in different parts of the In'yali-Debinsk zone and to 0.67% in the Ayan-Yuryakh zone. Systematic increase in CM content from coarse-grained to fine-grained rocks is found.

The average range in sandstones for the stratigraphic section is from 0.1 to 0.24%; in siltstones, from 0.24 to 0.69%; and in mudstones, it increases to 1.1%. The distribution of organic carbon in mudstones is near normal: histograms are bimodal with maxima at 0.4 and 0.8 to 1%. Siltstones are characterized by lognormal distribution of carbon with a mode between 0.2 to 0.4% and considerable dispersion in the rock. Sandstones are distinguished by insignificant dispersion of organic matter and lognormal distribution with a maximum between 0.1 and 0.15%.

No correlation between gold and organic carbon in sedimentary rocks was observed. Double correlation coefficients, calculated for both the entire region and individual stratigraphic sections, do not exceed 0.04-0.34.

Dispersion of the CM content is relatively minor in terrigenous rocks in all sections, and depends mainly on lithologic features. Against this relatively quiet background, a sharp increase in dispersion of CM content was observed in fault zones, especially in cases involving hydrothermal metasomatic processes, including gold mineralization. This was greatest in cases where the country rock was mudstone and siltstone, i.e., fine-grained rocks, in which graphitized CM was developed in deformed zones in the form of streaks and pockets of flakes and often CM-covered slickensides. The enrichment of certain parts of fault zones in carbonaceous material was apparently related to redistribution processes in the primary rock as a result of preore metamorphism. At the same time, a number of investigators [3] have shown that upon introduction of heat from intrusions in beds enriched in CM, a process of "burnout" and freeing of CO₂ and H₂O with liquid and gas-forming carbon creates a favorable environment for the migration of a number of microelements previously concentrated in the carbonaceous material. In our case, geophysical data on deep zones in ore areas has shown the presence of large, undiscovered granitoid intrusions.

At the same time, data on the composition of fluid inclusions in gold-bearing intrusive rocks and ore-bearing quartz [5] suggest a significant role for endogenic carbon, especially CO₂, in ore-forming processes. In this case, Paleozoic carbonate rocks at the base of the Verkhoysk complex can also be considered as a possible source of carbon and its compounds. These beds, which may have been assimilated by granitoids of the Kolyma and other complexes are all the more likely inasmuch as some of them are quite calcareous.

"Black shale" beds, characterized by high concentrations of CM, are favorable for localization of gold mineralization. But this factor should be considered from the standpoint of the role of dispersed organic matter as a regional geochemical barrier of reducing conditions that promotes the precipitation of gold from hydrothermal solutions. Aspects of the localization of gold mineralization in a number of cases indicates that the main role in this process is played not merely by a high CM content in rocks subjected to hydrothermal metasomatic activity, but its distribution, expressed by the high dispersion of CM content established by detailed studies of ore fields. This is indicated by the restriction of native gold segregates to the gouge of quartz, i.e., to contacts of units that contrast in CM content and in physical and chemical properties. Evidently under such circumstances the precipitational effects of CM as an active reducing agent are most effective.

This investigation has shown that although a high gold content is characteristic of the Verkhoysk complex, the effect of redistribution of *in situ* primary sedimentary gold by metamorphic processes is insignificant for the formation of gold ore deposits. The sedimentary beds may, however, be the source of ore material mobilized by granitoid intrusions.

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LITHOLOGICAL-PETROCHEMICAL AND GEOCHEMICAL FEATURES OF DEPOSITS HOSTING STRATIFORM GOLD MINERALIZATION IN SOUTHEASTERN YAKUTSK

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UDC 553.411.071(571.5)

On the basis of a combined geological-petrographic and petrological-geochemical analysis, the conditions of sedimentation and of post-sedimentary alterations of the beds of the Southern Verkhoyansk synclinorium hosting stratiform gold mineralization have been investigated. It has been shown that under the effect of thermodislocational metamorphism, an appreciable redistribution of the ore-forming elements takes place, thereby creating the objective conditions for gold to be concentrated in the stratiform quartz veins.

Over the past 20 years, gold-ore showings in carbonaceous terrigenous deposits, in particular stratiform gold-bearing quartz veins, have attracted ever greater attention. The concordant nature of such veins and the absence in the majority of the regions where they are found of any indication of magmatic activity are interpreted in various ways.

In discussing the conditions of formation of gold-ore bodies of this kind, they are classified either as diagenetic-sedimentary [15] or as syngenetic with the terrigenous sequence [6], which of course requires appropriate planning of the prospecting and exploratory operations.

According to the first hypothesis, the necessary condition for the formation of stratiform veins is considered to be the presence of kaolinite weathering crusts. It is suggested that as a result of the leaching away of the majority of the petrogenetic components, they are enriched to a significant extent in gold, which together with the dissolved silica is transported to the most deeply flexed parts of the synsedimentary depressions, which is where the gold-bearing stratiform veins preferentially form.

According to the second hypothesis, the gold is transported to the marine basin by underwater exhalations, and then in the process of settling out together with the amorphous silica and suspended fine-grained pelitic material is localized in quartz veins with a banded texture.

It appears fairly obvious that such a complete and precise, rhythmical differentiation in deposition can be realized only under a very slow and stable sedimentation regime. It is equally obvious that the clay-quartz rhythmic units (the banded veins) must in this case be located in the most finely grained parts of the terrigenous sequence. This work is devoted to a description of these mineralized occurrences in Southeast Yakutsk.

Structure of the Section and Petrographic Characteristic of the Terrigenous Rocks of the Region. Regardless of morphology, the majority of the gold-bearing occurrences of Southern Highlands are localized in the terrigenous rocks of the Lower Permian, consisting of a continuous section more than 2000 m thick.

In the northern and central parts of the region this is essentially a shale sequence, folded into a series of first-order cylindrical or box folds. In accordance with the insignificant amount of dislocation, the degree of alteration of the sedimentary rocks in these regions is no higher than the stage of catagenesis or the initial stages of the greenschist facies. In the north there are synsedimentary diabase sills distributed throughout the sedimentary rocks to a limited extent which underwent folding along with the terrigenous deposits [3].

Allakh-Yun'sk Geological Exploration Expedition. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 119-128, May-June, 1987. Original article submitted April 26, 1985.

TABLE 1. Mean Chemical Composition of Deposits of the Early Permian of the South Verkhoyansk Synclinorium, %

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	MnO	Na ₂ O	K ₂ O	H ₂ O	P ₂ O ₅	SO ₂	CO ₂	Calcina- tion loss	Total
Northern part															
Sandstones (5)															
70,4	0,54	11,7	3,95	0,10	1,04	1,88	0,06	3,99	1,06	0,10	0,20	0,12	4,01	—	100,05
Siltstones (27)															
62,61	0,68	15,43	6,86	0,80	2,33	1,87	0,06	3,11	2,95	0,37	0,17	0,30	2,05	—	100,00
Central part															
Sandstones (7)															
70,01	0,38	15,05	—	2,72	0,89	2,31	0,06	5,56	1,2	0,14	0,20	0,33	1,42	—	100,71
Siltstones (29)															
63,87	0,68	15,75	0,91	4,25	1,40	0,88	0,05	2,45	3,16	0,27	0,24	0,18	3,70	2,01	99,78
Southern part															
Sandstones (40)															
71,17	0,38	12,03	0,59	2,22	0,79	2,31	0,06	4,79	1,68	He oñ.	0,24	0,41	3,24	—	100,02
Siltstones (76)															
61,09	0,61	14,56	1,56	4,32	2,24	2,75	0,13	2,89	3,55	»	0,20	0,33	3,13	1,89	99,90

Note. Here and in the following tables the number of samples is given in parentheses.

TABLE 2. Petrological Moduli of the Terrigenous Rocks of the South-Verkhoyansk Synclinorium Calculated from Their Silicate Analyses

GM	FM	TM	SM	PM + SM	IM	IMM
Northern part						
Sandstones						
0,23	0,07	0,05	0,34	0,51	0,41	7,6
Siltstones						
0,38	0,16	0,04	0,20	0,39	0,78	11,35
Central part						
Sandstones						
0,26	0,05	0,02	0,37	0,45	0,18	7,3
Siltstones						
0,34	0,10	0,04	0,15	0,35	0,32	7,66
Southern part						
Sandstones						
0,21	0,05	0,03	0,40	0,54	0,23	7,5
Siltstones						
0,34	0,13	0,04	0,20	0,44	0,40	9,8

Sandstones in the form of isolated strata and thin groups of strata are encountered here only episodically and do not have an appreciable effect on the petrophysical and petrological-geochemical features characterizing the sections.

These are quartzofeldspathic or polymict fine-to-medium-grained rocks with lenticular-layered or turbulent textures, evidence of the exceptionally unstable conditions under which sedimentation occurred.

Petrographic examination shows, in addition to the quartz and feldspars, up to 20% of fragments of acidic extrusives and recrystallized volcanic glass. The fragmental material is angular and poorly sorted by size. The plagioclase in them corresponds to an albite-oligoclase composition, more rarely oligoclase-andesine, and fragments of it, just as the fragments of the volcanic rocks, are altered to different degrees: they are sericitized or replaced by a fine-grained aggregate of low-iron carbonate. The quartz fragments are frequently strongly deformed and exhibit undulatory or mosaic-block extinction.

The cement of the sandstones is carbonaceous-clay type, its clay component usually being weakly recrystallized and converted into finely scaley aggregate of light hydromicas. Because of the textural heterogeneity of the rock, the amount of cement varies over a wide range (5-30%), so that the type of cementation of the sandstones varies from conformo-regenerational or film-type to basal, which predominates in the high-limestone types.

Siltstones comprise the lower part in the northern and central sections of the region and are represented by black (carbonaceous) coarsely platy varieties of parallel, lenticular-layered or massive texture.

Approximately 60-70% of these siltstones consist of predominantly quartz fine clastic material. In addition to the quartz, oligoclase, microcline, acid lavas and platelets of strongly hydrated biotite have been identified in the clasts. The clastic material is poorly rounded, the cement of the siltstones is carbonaceous clay or limey-clay of the basal type. The quantity of limestone cement in different thin sections varies from 5 to 10%, even though in some beds and lenses its content may be as high as 25%.

The carbonaceous material is distributed relatively uniformly throughout the siltstones as serves as the pigment responsible for the black color of the rock. It is frequently segregated in the form of small lenses or angular clasts that can be seen to be highly deformed plant fossils exhibiting an indistinct cellular structure. The mean organic carbon content as determined from 38 quantitative analyses is 1.98% with a variation of 0.7 to 2.94%. No statistically significant correlations between the amount of organic carbon and gold in unaltered siltstones was found using the method of rank correlation ($r = -0.18$); in the

TABLE 3. Mean Contents of the Most Widespread Trace Elements in the Terrigenous Rocks of the South Verkhoyansk Synclinorium, $n \cdot 10^{-3}\%$

Ti	V	Co	Ni	Cu	Zn	Ga	As	Mo	Ag	Pb	Sb	P	Cr	Ge	Bi	B	Mn	Se	Zr	Ce	La	Th	Au*
Regional background of the South-Verkhoyansk synclinorium																							
Sandstones (1628, Au 211)																							
275	6	0,9	1,8	3,1	9,0	2,6	6,0	0,1	0,03	2,0	0,4	70	5	0,1	0,2	4	20	2	30	20	1	11	0,0
Siltstones (3936, Au 829)																							
243	7	0,9	2,4	4,7	14	3,4	7,0	0,2	0,05	2,9	0,6	100	4	0,2	0,2	2	8	2	20	10	1	9	7,2
Productive beds of the Early Permian																							
Sandstones (200, Au 127)																							
155	6	0,6	2,3	3,1	14	1,9	7,0	0,07	0,07	1,5	0,2	70	4	0,2	0,3	7	34	3	30	20	1	7	10,0
Siltstones (1500, Au 433)																							
456	9	0,9	1,8	5,7	13	1,9	10	0,1	0,05	2,9	0,9	50	9	—	0,5	7	60	—	20	20	1	7	12,2
Concretions of trachytes in the productive beds of the Early Permian (27, Au 27)																							
150	6	4	4	55	70	1,9	40	0,8	0,9	30	0,2	—	4	0,2	0,5	—	—	—	—	—	—	—	350,0
Clarke values in the productive beds of the Early Permian																							
Sandstones																							
1,03	3	20	11,5	6,2	8,75	1,6	70	14	10	2,1	4	4,1	1,1	0,2	—	2	0,85	30	1,87	2,2	0,3	—	4
Siltstones																							
0,99	0,69	0,47	0,26	1,27	1,37	1,0	77	0,04	10	1,4	1,5	0,7	1,0	—	—	7	0,7	?	1,0	3,3	0,14	5,8	4,88

Mean gold contents in mg/ton; Clarke values taken from [19].

TABLE 4. Dependence of the Co/Ni Ratio on the Degree of Metamorphism of the Ore Host Beds

Position of the part of the section tested in the host rocks	Rocks	Co/Ni
Key beds beyond the metamorphic belts	Sandstones Siltstones	0,26 0,50
Sections in the zone of weakly expressed metamorphism (chlorite subfacies level in the third megarhythm)	Sandstones Siltstones	0,53 0,57
Sections in the zone of the most intensively expressed metamorphism (biotite subfacies level in the first megarhythm)	Sandstones Siltstones	4,70 0,04

quartzified fold belts the negative sign is retained, but the absolute value of the corresponding coefficient increases to 0.52 at the 99% confidence level.

The catagenically altered shales in the northern and central regions of the South Verkhoyansk synclinorium have the highest effective porosity (2.68%) and reduced elastic properties, making them most favorable for localizing the gold mineralization.

The argillites, which here form the upper half of the Lower Permian section, are represented throughout by black, carbonaceous-argillitic varieties. In comparison with the underlying siltstones, they are more elastic, have a very low effective porosity (0.32%), and serve as the regional thermodynamic and geochemical screen [13, 14].

The structure of the lower half of the Lower Permian section underwent rather substantial alterations of the given set of terrigenous rocks which increases with the amount of displacement in the southern direction. It exhibits here a clearly defined cyclicity consisting of several megarhythms around 500 m thick. They all begin with psephitopsammitic beds and end with groups of beds of silty-pelitic composition.

The lower, coarse-grained horizons of the megarhythms exhibit highly variable thicknesses and impersistence in their granulometric composition. Typical of these rocks are numerous local discontinuities or disconformities with a wide variety of textures.

Among the other lithological varieties here, tilloid types of siltstones are common. These contain irregularly distributed pebbles or clasts of the most varied petrographic composition and represent typical turbulent flow turbidite deposits [2].

The structure of the section is evidence of an active and extremely unstable hydrodynamic regime in the marine basin where the terrigenous sequence basically represents delta facies and which developed under conditions of avalanche sedimentation, in the terminology of A. P. Lisitsyn [7].

It is to these extremely unstable and mechanically heterogeneous parts of the megarhythms that the stratiform gold-quartz showings are confined in the southern part of the region. Within the lithologically contrasting Lower Permian sequence their position is controlled by linear belts of intensified dislocations, which trace the deeply penetrating faults in the basement [1].

In connection with the appearance here of small-scale, very tight folding at the level of the localization of the stratiform gold-bearing occurrences there is a fundamental alteration of the structural-textural appearance of the terrigenous rocks without any appreciable change in their mineral composition. Such relationships show that the transformation of the rocks hosting the ore in connection with the linear folding occurred in this region under the high pressures and moderate temperatures of thermodynamical metamorphism [8].

Only about 20% of the thickness of the southern sections is accounted for by sandstones and gravellites, but due to their coarse grain size they provide the most objective information about the petrographic composition of the primary sediment and the changes it underwent during metamorphism. At the base of the first megarhythm, the sandstones and gravellites are represented by poorly sorted quartzofeldspathic and polymict varieties, as a rule, chloritized and sericitized to different degrees.

These are slaty rocks having gneissic, more rarely augen-gneissic, microtexture with a usually poorly sorted granuloblastic structure of the clastic material, and at times, of the

TABLE 3. Mean Contents of the Most Widespread Trace Elements in the Terrigenous Rocks of the South Verkhoyansk Synclinalorium, $n \cdot 10^{-3}\%$

Ti	V	Co	Ni	Cu	Zn	Ga	As	Mo	Ag	Pb	Sb	P	Cr	Ge	Bi	B	Mn	Se	Zr	Ce	La	Ta	Au*
Regional background of the South-Verkhoyansk synclinalorium																							
Sandstones (1628, Au 211)																							
275	6	0,9	1,8	3,1	9,0	2,6	6,0	0,1	0,03	2,0	0,4	70	5	0,1	0,2	4	20	2	30	20	1	11	6,0
Siltstones (3936, Au 829)																							
243	7	0,9	2,4	4,7	14	3,4	7,0	0,2	0,05	2,9	0,6	100	4	0,2	0,2	2	8	2	20	10	1	9	7,2
Productive beds of the Early Permian																							
Sandstones (200, Au 127)																							
155	6	0,6	2,3	3,1	14	1,9	7,0	0,07	0,07	1,5	0,2	70	4	0,2	0,3	7	34	3	30	20	1	7	10,0
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Concretions of trachytes in the productive beds of the Early Permian (27, Au 27)																							
150	6	4	4	55	70	1,9	40	0,3	0,9	30	0,2	—	4	0,2	0,5	—	—	—	—	—	—	—	350,0
Clarke values in the productive beds of the Early Permian																							
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1,03	3	20	11,5	6,2	8,75	1,6	70	14	10	2,1	4	4,1	1,1	0,2	—	2	0,85	30	1,87	2,2	0,3	—	4
Siltstones																							
0,99	0,69	0,47	0,26	1,27	1,37	1,0	77	0,04	10	1,4	1,5	0,7	1,0	—	—	7	0,7	?	1,0	3,3	0,14	5,8	4,88

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cementing material as well. Depending on the ratio of these, the textural picture of the sandstones and gravellites is determined either by the directional orientation of the extended lenticular clasts, or by the striation pattern of the quartz-chlorite-sericite basal-film cement of the granolepidoblastic structure.

During dislocational metamorphism, the cement and clastic component underwent substantial restructuring, so that today in the rocks of psephitopsammitic size, conformal-regenerational or incorporation type cementation predominate.

Clastic material in these rocks accounts for 70-80% of the total. Most extensively developed are the weakly rounded clasts of medium (No. 30-35) plagioclases, siltstones, and acidic lavas (30-70%). These are followed by quartz (20-30%), potassic feldspar (up to 5%), usually strongly albitized, and allogenic biotite (up to 1%). Among the accessory minerals sphene, zircon, ilmenite, cassiterite, and rarely, garnet, have been identified. Authigenic minerals in the gravellites and sandstones include a quite variable amount of chlorite, sericite, and albite, the total of which reaches 30% in some thin-sections.

Moving up through the section, the composition of the clastic material becomes markedly more simple, and quartz sandstones containing 10-20% of acidic (No. 10-15), more rarely intermediate (No. 30-35) plagioclase in clasts predominate, the sandstones being virtually free of volcanomictic material.

The siltstones in the southern part of the region, regardless of their position in the lithologically contrasted part of the section, are represented by carbonaceous-argillaceous varieties with parallel or lenticular-layered texture. The basic fabric of the rock, like the clasts scattered through it, is sericitized. The sericite is developed especially strongly in the siltstones of the first megarrhythm, where its segregations have a finely aggregational or lepidoblastic structure, which sharply interferes in the red and blue colors of the first order and emphasizes the slatiness of the rock.

Under the action of thermidislocational metamorphism the bituminous component of the organic matter disseminated throughout the rock apparently undergoes natural cracking and segregates in quartz-anthracolite veins. On the basis of spectrochemical determinations, the anthracolite of these veins may contain up to 3 g/ton of gold.

The previously mentioned tilloid siltstones of turbidite origin occupy a specific position in the southern sections. Among the clasts and poorly-sorted pebbles they contain the following, in order of decreasing frequency, have been identified: recrystallized limestones, rhyolites, acidic plagioclase and albitized microcline, i.e., the same components as in the psephitopsammitic sediments.

Based on the descriptions given above, all these rocks must be considered to be the product of altered terrigenous sediments, moderately well or poorly sorted by composition and extremely unsorted in terms of the size of the clastic material. They are formed as a result of a single cycle of erosion of a juvenile or moderately mature sequence in which volcanic rocks of acidic (dacite-rhyolite) composition played an important role. No petrographic signs of synsedimentational volcanism were detected in them.

Petrochemical and Geochemical Features of the Terrigenous Rocks. In order to provide a more complete answer to the question of the conditions of sedimentation in the Early Permian basin and the composition and degree of maturation of the rocks of the distributive provenance, we used the results of 184 analyses of samples taken from the sections in three traverses covering the north, center and south of the region and 150-200 km apart (Table 1). All the samples for characterizing the petrochemical and other properties of the terrigenous rocks, were taken in exposures or exploration shafts devoid of ore mineralization.

It follows from Table 1 that compositionally similar varieties of the sections studied do not differ substantially in the content of their petrogenetic minerals. The most important factor is the strong dewatering of the sandstones and siltstone of the southern sections, which is associated with their position in the belt of intensive thermidislocational metamorphism.

In order to make a quantitative assessment of the role of the clastic material of different origins and the completeness of the separation of the petrogenetic components in the course of sedimentation and the subsequent restructuring of the sedimentary sequence, a number of petrological moduli were calculated (Table 2). Comparative analysis [18] shows that in estimating the degree of weathering and the completeness of the separation of the products of the

hydrolysis and the silica of the terrigenous rocks, the modulus having the greatest resolving power is $GM = (Al_2O_3 + TiO_2 + Fe_2O_3 + FeO)/SiO_2$. In our case its median value is no greater than 0.34, which according to Ya. E. Yudovich, is characteristic of normal terrigenous deposits such as polymict sandstones that have not undergone hydrolysis.

A weakly expressed tendency for the hydrolysis products to be removed is also indicated by the low values of the femic $FM = (FeO + Fe_2O_3 + MgO)/SiO_2$ modulus, and especially of the titanium modulus $TM = TiO_2/Al_2O_3$. The value of the latter varies within limits of 0.02-0.05 with a median value of 0.04. The very low value of this parameter and its narrow range of variation are typical of poorly sorted terrigenous sediments that have not undergone reworking of the terrigenous sediments.

The median value of the sodium modulus $SM = Na_2O/Al_2O_3$ in this case is close to 0.34, which also points to insignificant weathering of the plagioclases and is in good agreement with the conclusion that hydrolysis played a minor role.

The overall potassium-sodium modulus $PM + SM = (K_2O + Na_2O)/Al_2O_3$ reflects a normal or somewhat elevated alkali content of the sediments under investigation. For the northern part of the region, where the alkalinity is somewhat higher, the iron modulus $FeM = (FeO + Fe_2O_3 + MnO)/(Al_2O_3 + TiO_2)$ of the siltstones rises. This fact is accounted for by the appearance of basitic magmatism simultaneously with them (cf. above), which is entirely lacking from the central and southern parts of the territory, where elevated alkalinity has been established in beds that are normal in terms of iron content.

In addition to the petrological moduli, which are well suited for studying the petrochemistry and geochemistry of the sedimentary sequence of the Pripolar Urals [18], the iron-manganese modulus is greater than 20. For the terrigenous rocks of the South Verkhoyansk synclinorium this parameter, calculated using the data and individual analyses, is as a rule less than 10. A natural exception once again is provided by the siltstones of the northern sections (IMM 11.35), but here too it lies within the field of ordinary marine sediments (IMM 10-20).

The composition and concentrations of microcomponents in the terrigenous rocks of the Lower Permian have been characterized from the results of 17,000 semiquantitative spectroscopic analyses performed using a DFS-8 spectrograph and the data of 1067 radiochemical determinations of gold. This information is summarized in Table 3, where for comparison we also present information on the regional background levels of rocks of the entire terrigenous complex, from the Upper Carboniferous to the Lower Jurassic inclusive, and the Clarke values for the ore elements in the individual lithological varieties.

The most important feature of the sections we are considering is their sharply elevated arsenic content, which serves as a profiling element for the gold-bearing veins of the region, being found in arsenopyrite and arsenic geochemical types of low-sulfide gold-quartz formations [10]. Such specialization of sedimentary rock and ore showings is an expected result of their location within the arsenic geochemical province [4, 5].

From the data presented it also follows that in comparison with the planetary Clarke value, the sandstones of the region are enriched to some extent in the great majority of ore-forming elements. This phenomenon may be explained either by their clastic-mineral nature, or by the sorptive property of the sandstones that take up the ore substance in the process of catagenic-metamorphic alterations of the terrigenous rocks.

The latter of the alternatives appears to us to be the more realistic, since even in the belts of thermotectonic metamorphism, where the petrophysical properties are leveled out to a significant extent, the effective porosity of the sandstones still remains 1.7 times higher than that of the siltstones (0.55 and 0.32%, respectively). On the basis of the gold content as measured against the regional background of the South Verkhoyansk synclinorium, the productive beds of the Lower Permian stand out markedly, the level of enrichment in the noble metal being approximately the same for both the sandstones and the siltstones here.

Within the limits of the Lower Permian section, the unmetamorphosed sandstones and siltstones differ little in gold content, even though its concentration level is somewhat higher in the rocks of the siltstone dimension. A significant contribution to the overall balance of the noble metal here is made by marcasite concretions, and metacrystallized pyrite is also developed, both of which are distributed throughout the Lower Permian siltstones and contain on the average 0.35 g/ton of gold [11]. Iron disulfides are in general excellent

concentrators of a broad spectrum of ore-forming elements and more clearly reflect the geochemical specialization of sedimentary rocks [12].

A diametrically opposite picture of the distribution of gold between the sandstones and the siltstones appears in the belts of thermidislocational metamorphism that control the disposition of stratiform-type gold showings.

Here, in sandstones of the first megarhythm, the gold concentration is 10 mg/ton, whereas in the siltstones its content does not reach 1 mg/ton. For the third megarhythm, located 500 m higher up the section, the corresponding values are 90 and 12 mg/ton.

In our opinion, this disproportion is the result of a metamorphic redistribution of the primary gold concentrations. In the course of this process, groups of more porous sandstones served as collectors, and the siltstone parts of the Lower Permian section became the productive parts.

This interpretation is confirmed by data presented above on the natural cracking and the redeposition of the organic matter, and also the sharp change in the value of the Co/Ni ratio in rocks that have undergone the highest degrees of metamorphism (Table 4).

It is readily noted that in the less altered rocks of the third megarhythm the value of the modulus is of the same order as it is outside the metamorphic belt. On the other hand, in the section of the first rhythmic group, where the metamorphism was more intense, the ratio of the elements of interest to use is an entire order of magnitude greater. This is due exclusively to the redistribution of the most mobile element, cobalt, which like gold is transported from the ore source rocks and enriches the collector beds. While the cobalt undergoes regrouping only at the bottom part of the productive section, the gold is also extracted at the higher (third megarhythm) structural-hypsometric levels during migration. This relationship is the objective result of the thermodynamic properties of the elements we are comparing [9]. As the more mobile element, gold is transported over greater distances, and then is concentrated not only in the collector beds of the sandstones, but in the quartz veins of the concordant type.

* * *

In summary, the following conclusions can be drawn:

The deposits of the Lower Permian of the South Verkhoyansk synclinorium represent normal marine terrigenous sediments formed as a result of an intense single cycle of weathering of barely mature rocks, among which acidic volcanics were extensively developed. Sedimentation occurred here under the extremely unstable conditions of a delta facies periodically subject to avalanches, which was responsible for the high degree of lithological variability of the productive part of the section, in which the rocks did not pass through the stage of crust formation later in the course of their evolution.

The restriction of the stratiform gold showings to the coarse-grained lithologically heterogeneous sediments that had not undergone hydrolysis rules out the possibility of their syngenetic formation; they were enriched in gold and the major ore-forming elements which were distributed throughout the entire Early Permian sequence from the beginning.

Dewatering of the terrigenous sequence and its clearly expressed regrouping of gold and other elements by the processes of thermidislocational metamorphism create the preconditions for the formation of epigenetic concentrations of the noble metal. The mechanism of such concentrations in accordance with the postulates of the metamorphic-hydrothermal hypothesis have been discussed in detail in the numerous publications of V. A. Buryak and are not the subject of this article.

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DOLOMITE TYPES IN THE UPPER JURASSIC OIL AND GAS DEPOSITS OF SOUTHERN TURKMENIA

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UDC 552.543(575.4)

Various types of dolomite collector rocks found amid oil and gas deposits of the Upper Jurassic in southern Turkmenia are described.

Carbonate oil and gas deposits in many regions of the world are represented by dolomites; some dolomite varieties are high-capacity porous collectors, while others are fluid-resistant. For efficient geologic and gas prospecting in these regions a comprehensive and detailed study of oil and gas deposits is necessary, including the determination of the genesis of these rocks and the influence of postsedimentary alterations on their current habitus. Soviet and foreign investigators have studied these issues for many years. Genetic diagnostics of dolomites, however, is not fully developed, and many of its aspects remain debatable.

The present paper analyzes the formation conditions of dolomites in an attempt to define the lithologic features of their genetic diagnostics as they apply to the specific environments of southern Turkmenia, with special reference to Sabur oil and gas deposit, Kyrk gas deposit, and oil and gas exploration areas Chirli and Karamaya. The Upper Jurassic (Callovian-Oxfordian) rocks of the area are organogenic-detrital, often dolomitized limestones, and

All-Union Scientific-Research Petroleum Geologic Exploration Institute, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 129-135, May-June, 1987. Original article submitted March 24, 1986.



Fig. 1

Fig. 1. Sedimentary dolomite: hole Kyrk-1 (depth 3910-3930 m), crossed nicols, magnification 100×.

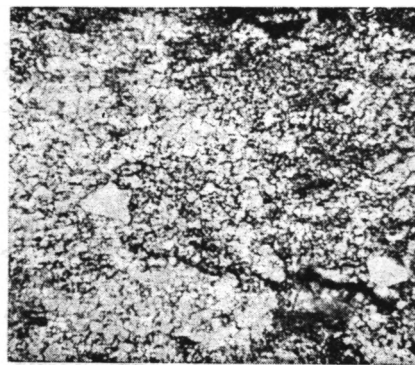


Fig. 2

Fig. 2. Dolomite of diagenetic replacement of limestone: hole Chirli-1 (depth 3878-3884 m), single nicol, magnification 100×.

dolomites with anhydrite interlayers overlain disconformably by Lower Cretaceous terrigenous-carbonate rocks of the Neocomian complex. The dolomites account for about half of the Upper Jurassic profile, and these are the beds containing small oil and gas deposits and numerous oil and gas shows.

The study has identified three morphologic-petrographic dolomite types which can be interpreted as stadal-genetic types: 1) sedimentary dolomites; 2) diagenetic dolomites replacing carbonate ooze; and 3) catagenetic dolomites replacing limestone.

Sedimentary Dolomites are gray, light-gray, and brownish-gray rocks with a fine-grained structure (rhombohedral grains about 0.01 mm) of imperfect crystalline form and ubiquitous inequigranularity (Fig. 1), indicating the single-stage character of their crystallization. Tatarskii [6] believes that these could be carbonate grains precipitated from solution and formed during diagenesis of the sediment, probably mainly in the early diagenetic stage. Some of the rock specimens include dolomite rhombohedra of 0.02-0.08 mm; these grains occur at random, accounting for 1-2% of the rock. In the rock specimens of this type that have been studied, no faunistic remains have been recorded (such as ostracod and foraminiferal shells). At the contact between anhydrite and the enclosing fine-grained dolomite matrix, dolomite rhombohedra of 0.01-0.05 mm have been described. In sedimentary dolomites a clay impurity and terrigenous fragments, mainly of a silt size, are found, accounting for up to 45% of the content. The terrigenous material is represented largely by quartz fragments, with feldspars playing a minor role. Pyrite segregates are found as single grains or aggregations, ranging in size from a few one-hundredths of a millimeter to 0.2 mm. Pyrite is sometimes oxidized, coloring the rock brownish. Sedimentary structures such as drying cracks and wave ripple traces are well preserved. Sedimentary dolomites interstratify with anhydrites, in which they occur as lens inclusions and interlayers, from a fraction of a meter to several meters thick; they are also found as interlayers in diagenetic dolomites. Sedimentary dolomites are mostly dense varieties, with a porosity less than 1%; they contain very thin (<0.01 mm) primary intergranular pores with little interpore communication.

Sedimentary dolomites in the Upper Jurassic of southern Turkmenia have thus been identified by the following features: a) a fine-grained rock texture typical for grains directly precipitated from solution; b) absence of any traces indicating a replacement by dolomite of preexisting carbonate ooze; c) shallow sea settings of sediment formation (the presence of drying cracks and traces of wave ripple and oxidized iron compounds); and d) salinization of the sedimentation basin in an arid climate (the association of this type of dolomite with anhydrites and conditions unfavorable for life).

The low primary porosity of the sediments was responsible for limited development of postsedimentary alteration in them. During the late diagenesis, the slightly lithified sediment experienced little recrystallization, forming dolomite rhombohedra of 0.02-0.08 mm. Subsequently (late diagenesis-early catagenesis), the rare faunistic remains found in the rock experienced lixiviation; pore walls became encrusted with rhombic dolomite grains of 0.02-0.07 mm, with lixiviation pore volume not exceeding 1-2% of the rock. Sulfatization has had

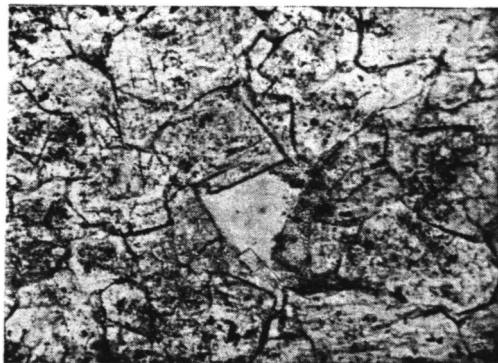


Fig. 3. Dolomite of catagenetic replacement of limestone: hole Karamaya-1 (depth 3035-3043 m), single nicol, magnification 100 $\times$.

a strong influence on the current habitus of sedimentary dolomites. During catagenesis, anhydrite filled pores and cracks formed by bed deformation; it replaced metasomatically the adjacent portions of the matrix, further worsening the infiltrational properties of the rock.

Dense sedimentary dolomites associated with anhydrite interlayers now appear as relatively thick (several tens of meters) impermeable members, which can be regarded as zonal or local fluidcluses, likely to screen hydrocarbon deposits. These rock associations are particularly common in the top of the Upper Jurassic profile.

Diagenetic Dolomites Replacing Carbonate Ooze are rocks similar macroscopically to the sedimentary dolomites described above. They, too, are of a gray, light-gray, and brownish-gray color. Diagenetic dolomite grains measure 0.01-0.05 mm, sometimes slightly larger, and are mainly of a rhomboid or irregular quasirhomboid shape. The largest grains (0.03-0.05 mm) in microscopic investigations in transmitted light appear of a lighter pigmentation than smaller grains; they are spread unevenly throughout the rock, sometimes as irregularly shaped accumulations. Merging locally, these accumulations form a "mosaic" rock structure, resulting in the uneven pigmentation of the rocks (Fig. 2). Clay and terrigenous impurities are frequent in diagenetic dolomites. Terrigenous matter ranges from single inclusions to 35% of the rock; it consists mainly of silt-sized inclusions. As the fragment sizes increase, their sorting deteriorates. Like in sedimentary dolomites, quartz fragments are predominant; feldspar fragments are much less frequent. In individual specimens fragments of dolomite and sedimentary silica with the maximum size of 3 mm are found. Anhydrite segregations are contained in all specimens studied (from 1 to 40% of the rock). Spotty, irregularly shaped areas of primary fine-grained limestone are found in dolomites of this type. Fine-grained calcite (grain sizes of 0.01 mm and less) is present also as rounded or oval pellets. Echinoderm, brachiopod shell, and bivalve remains of various degrees of preservation are found in the rock. Pyrite content varies from single inclusions to 1%; in some dolomite varieties iron compounds are oxidized, endowing the rock with a brownish color. Diagenetic dolomites are mostly low-porosity varieties (1-3%); dense varieties (<1%) are less frequent, with porous varieties (3-7%) of this type playing a clearly subordinate role. Two types of pores are distinguished: pores of lixiviation of faunistic remains and intergranular interstices. Lixiviation pores range in size from a few one-hundredths of a millimeter to 0.7 mm; they are of an oval or elongate shape, similar to that of faunistic remains common in the Upper Jurassic limestones. Pore walls are often encrusted with dolomite rhombohedra of 0.05-0.1 mm; such grains fill the interstitial space fully or partially. Intergranular pores (0.01-0.03 mm) play a subordinate role in the volume of the interstitial space; they account for less than 1% of the rock in most cases. In individual rock varieties, small-amplitude sutures and desiccation cracks filled with anhydrites are observed. Diagenetic dolomites occur in association with anhydrites and sedimentary and catagenetic dolomites; they are found as lenses and beds, from a fraction of a meter to 15 m thick.

This type consists of dolomites formed by the replacement of primary calcareous ooze with dolomite during sediment lithification. The following features identify this rock type: a) the presence of areas of primary fine-grained limestone in this dolomite type; b) the fact that dolomites of this type often are transient varieties between sedimentary dolomites, characterizing a high salinity sedimentation basin, and dolomites of the catagenetic replacement of organogenic detrital limestones, formed in sedimentation settings of normal salinity marine basins; and c) small-grained rock texture. Tatarskii [6] notes that small-grained texture (0.01-0.05 mm) is probably impossible for a carbonate precipitating as sediment from waters of the basin. It is representative mainly of diagenetic carbonate. In rare instances,

such oozes could be produced by epigenesis, mainly near the upper limit of this size range [6].

An analysis of the available data and the relationships in the occurrence of the diagenetic dolomites and their enclosing rocks suggests that primary limestones were deposited mainly in a shallow marine basin, largely of normal salinity and in relatively calm hydrodynamic environments. Periodic increases in the intensity of the hydrodynamic regime were accompanied by increased inflow of terrigenous matter and deterioration of fragment sorting in the sedimentation basin.

The lithification of sediments took place both in the course of the diagenesis proper and as a result of exodiagenesis, as indicated by the presence of drying cracks in individual samples. Strakhov [5] noted that a slightly lithified ooze during diagenesis is characterized by unevenness of the geochemical conditions in individual near-lying parts of the sediment (the unequal pH and Eh of the medium); these differences are due to uneven partial pressures of CO₂ and uneven distribution of organisms in the ooze, especially the discreteness of bacterial populations and various forms of organic matter. Such conditions could be responsible for the uneven concentration of magnesium ions in individual portions of the ooze, resulting in an uneven dolomitization of the sediment. The source of magnesium for dolomitization of calcareous ooze was probably supplied as ions from overlying sedimentary-dolomitic and evaporitic sediments. Dolomitization developed sometimes partially, but sometimes with a complete replacement of primary ooze and shape components. The dolomitization of calcareous ooze during diagenesis resulted in intergranular interstices formed in the rock.

Later catagenetic processes were superimposed on diagenetic processes of dolomite formation. The bulk of the interstitial space in diagenetic dolomites was probably formed during the late diagenesis-early catagenesis by lixiviation of rock components, primarily faunistic remains. The pore walls were later encrusted with newly formed dolomite rhombohedra, slightly decreasing the pore volume in the rock. Subsequent sulfatization processes further reduced the volume of void space; anhydrite grains filled partly or completely the preexisting rocks and cracks in the rock and reduced the communication between the voids. The rock dissolution under heightened pressures formed small-amplitude sutures in some of the varieties of diagenetic dolomites.

Dense diagenetic dolomites, which could function as a reliable fluidiclude, occur relatively infrequently, which is also true of the varieties that could be collectors of hydrocarbons. The most common rocks are of a low porosity (1-3%), suggesting that diagenetic dolomites should be mainly regarded as intermediate strata of dispersion of hydrocarbons inside oil and gas reservoirs along the hydrocarbon migration routes.

Catagenetic Dolomites of Limestone Replacement are the most widespread variety in the Upper Jurassic of southern Turkmenia; they form relatively thick beds (from several meters to 100 m and more). This dolomite type occurs sometimes on thinner interlayers interstratified with diagenetic and sedimentary dolomites.

Catagenetic dolomites are lighter in color than the dolomites of the foregoing two types. Grains are mainly of 0.05-0.2 mm in size, of a rhombohedral and irregular rhombohedral shape (Fig. 3). Both inequigranular and comparatively equigranular varieties are found in the profile studied. Microgranular carbonate pellets are frequent inside some of the rhombohedra. Many of the varieties of this dolomite type contain primary limestone segments and faunistic remains. Terrigenous impurities are much less frequent than in sedimentary or diagenetic dolomites; sometimes they are absent. The contents of terrigenous matter rises at contact with diagenetic dolomite, sometimes up to 45% of the rock. Anhydrite is found in all specimens studied (1-15% of the rock); it fills interstitial spaces and replaces adjacent matrix portions. Chalcedony is found in the pores of some of the rock varieties. Pyrite content in catagenetic dolomites is lower (isolated inclusions) than it is in sedimentary and diagenetic dolomites. Singular glauconite grains are sometimes found. The porosity of catagenetic dolomites in the specimens studied ranges from a fraction of one percentage point to 20%. Two types of cavities are observed: intergranular pores and voids from lixiviation of faunistic remains. Intergranular pores account for at most 2-3% of the rock; they are of a characteristic angular shape and a size from 0.01 to 0.1 mm. The main volume of the void space consists of pores and caverns of faunistic remains lixiviation. The voids of this type are of 0.03-5 mm; they are of a rounded, oval, elongate, slotlike, or crescent shape, inherited from shells dissolved by leaching. With increasing rock porosity, the degree of their dolomitization grows regularly. The walls of cavities are often encrusted by larger dolomite rhombohedra, which have a lighter color in transmitted light (compared with the matrix).

Sedimentary and diagenetic dolomites are typical for sedimentation facies and sediment lithification settings; they have similar features which sometimes make the diagnosis difficult. Catagenetic dolomites were formed by postsedimentary processes acting on limestones formed previously in different facies. The type of dolomitization depends on the primary composition and structure of limestones and physicochemical conditions under which limestones and physicochemical conditions under which limestones were replaced. Due to the wide diversity of these environments, the textures of catagenetic dolomites are much more diverse than those of sedimentary and diagenetic dolomites. Catagenetic dolomites often inherit the texture of the primary limestone. Based on these features and on analogy with similar textural limestone varieties found in a section, one can reconstruct at least partially the conditions of their sedimentation and the sequence of secondary alterations that preceded dolomitization.

The accumulation of calcareous ooze, which provided the parent matter for dolomites, probably took place in a shallow marine basin of normal salinity with relatively calm hydrodynamics.

Later, during the late diagenesis-early catagenesis, the Upper Jurassic rocks were subject to lixiviation, which produced cavity space.

Limestone dolomitization had a major impact on the current habitus of the Upper Jurassic in southern Turkmenia. The principal agents of dolomitization were brines of evaporitic rocks overlying the limestones. The theory of catagenesis of the sedimentary rocks underlying evaporitic and homogeneous beds had been worked out by numerous investigators [2-4, 7, 8, and other publications]. The gist of this theory is the assertion that in the gravity field of the earth, liquids of a higher density tend to migrate toward a lower position in the profile relative to liquids with a lower density. The brine of evaporitic sediments, which is the end result of seawater metamorphism in an arid basin as it is separated from evaporitic beds, seeped slowly into underlying limestone. According to Valyashko, Polivanova, and Zherebtsova [1], the heavy fluids flew downward and the light fluids upward in jets through beds; this was confirmed by their experimental studies. Sulfatization of beds is presumably associated with the intrusion of brines into locally weakened, in particular, cracked zones; this may be accompanied by hydraulic rupture and migration of the brine "spreading" laterally (in the more permeable collector beds). At the brine-rock contact the geochemical environment changed, complex ion exchange reactions took place, and limestones were dolomitized, forming the products of the Heidinger dolomitization reaction: $2\text{CaCO}_3 + \text{MgSO}_4 = \text{CaMg}(\text{CO}_3)_2 + \text{CaSO}_4$.

A key significance of brines of anhydritic beds in limestone dolomitization is confirmed by the fact that evaporitic beds are usually underlain by dolomites. Limestones occur over evaporites. Dolomitization could be partial or lead to a complete replacement of limestone. The intensity of dolomitization decreases in proportion to the distance from evaporitic beds and inversely to porosity of limestones that were dolomitized. During the early catagenesis, the walls of pores and caverns were encrusted with grains of newly formed dolomite, which to some extent reduced the volume of the interstitial space of catagenetic dolomites.

The sulfatization of rocks was probably simultaneous with their dolomitization. Anhydrite filled pores to various degrees and replaced the adjacent components of the matrix. Catagenetic silicification of dolomites was limited. Chalcedony has been found in just a few of the rock specimens investigated. A partial dissolution of carbonate matrix under high pressures produced small-amplitude sutures in catagenetic dolomites.

Although the dolomite types described are the principal types in the Upper Jurassic of southern Turkmenia, intermediate varieties also occur in addition to these "pure" types.

Carbohydrate deposits identified in this territory in the Upper Jurassic are confined to dolomites of catagenetic replacement of limestones. The porous varieties of this dolomite type account for the main volume of the Upper Jurassic collector rocks. Low-porosity varieties of catagenetic dolomites and some varieties of diagenetic dolomites are intermediate strata of the dispersion of hydrocarbons in the natural oil and gas reservoirs on hydrocarbon migration paths.

Dolomites similar to those described in this paper could be widespread on adjacent territories, which have a similar geologic history. An accurate diagnosis of the stadiol and genetic types of dolomites and description of their occurrence in vertical and lateral sections must be useful for purposeful oil and gas prospecting in these territories and for raising the efficacy of exploration work.

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LITHOHYDROGEOCHEMICAL CRITERIA FOR PREDICTION OF INTENSE CATAGENETIC DOLOMITIZATION OF LIMESTONES IN HALOGENOUS-CARBONATE FORMATIONS

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UDC 552.543:552.53

With special reference to the Pripyat trough, a quantitative evaluation is obtained of the proportion of secondary porosity formed by interaction of inter-crystalline brines with carbonate rocks. The lithohydrogeochemical criteria for predicting areas where an intense catagenetic dolomitization of limestones is likely to occur in regions of development of halogenous-carbonate formations are defined: the presence of silvine-carnallite rocks and minerals of a higher degree of condensation of seawater in the overlying salt-bearing bed; and the presence, in carbonate complexes, of hydrogeochemical anomalies, manifested as heightened potassium and lowered magnesium content.

Dolomites have been the subject of a large number of publications by Soviet and foreign investigators, as these rocks form a large part of the sedimentary cover in many basins and are one of the most common oil-containing sediments.

Many of these studies discuss the genesis of dolomites and, in particular, catagenetic dolomitization of limestones. There has been far less work on the criteria for predicting the areas of likely intense development of this process and for evaluating the catagenetic dolomitization and its influence on the collector properties of carbonate in places of widespread salt-bearing strata.

The present paper evaluates the proportion of secondary porosity produced by interaction of subsalt and intersalt brines with carbonate rocks; we define new lithohydrogeochemical criteria for predicting the areas of intense catagenetic dolomitization of limestones in halogenous-carbonate formations. Pripyat trough is the area taken for illustration, where two thick Devonian salt-bearing beds (up to 3 km and thicker) are well developed, while carbonate rocks are widespread in inter- and subsalt beds. The territory is well explored by deep oil bore holes and by shallower bore holes for potassium salt.

Ukrainian Scientific-Research Institute of Petroleum, Gomel'. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 136-140, May-June, 1987. Original article submitted August 8, 1985.

TABLE 1. Calculated Amounts of Magnesium From Stratal Water Contributed to Secondary Dolomitization of Subsalt and Intersalt Carbonate Rocks

Types and stratigraphic characteristics of brines	Weight of components, 10 ⁹ tons				magnesium contributed to secondary dolomitization, mMg
	$\frac{Ca}{Mg}$	$m Ca^{++} + Mg^{++}$ [3]	Ca ⁺⁺	Mg ⁺⁺	
Parent brine of Frasnian halogenic basin	1,73	—	16,9	5,9	3,6
Stratal brines of subsalt deposits	5,4	22,8	20,5	2,3	
Parent brine of Famennian halogenic basin	1,59	—	19,8	12,5	8,8
Stratal brines of intersalt deposits	4,77	32,3	28,6	3,7	

TABLE 2. Estimate Proportion of Cavities Formed by Secondary Dolomitization of Subsalt and Intersalt Carbonate Rocks

Rock complex	Volume of cavities, km ³ [3]	Weight of magnesium from stratal waters spent in dolomitization, 10 ⁹ tons	Weight of secondary dolomite, 10 ⁹ tons	Volume of secondary dolomite, km ³	Cavity volume formed, km ³	Proportion of secondary cavities, %
Subsalt carbonate	290	3,6	27,7	11,0	1,4	0,5
Intersalt	539	8,8	68	27	3,4	0,6

According to the position with respect to the Frasnian and Famennian salt-bearing beds, the sedimentary cover is subdivided into undersalt, intersalt, and subsalt beds and two salt-bearing beds. The subsalt deposits are divided into two subbeds: the lower, clay-terrigenous, subbed and the upper, carbonate, subbed. The intersalt stratum on most of the territory consists of carbonate rocks. In the southern part of the trough terrigenous rocks are widespread; in the eastern part volcanogenic sedimentary rocks are more common. In the upper salt-bearing bed, within the northwest part of the region, potassium salts are prevalent; carnallite interlayers are much less frequent.

The intersalt and subsalt carbonate deposits of the Pripyat trough have experienced intense dolomitic metasomatism, most pronounced in the northern part of the region. The petrographic evidence of the predominantly catagenetic nature of these dolomites in this area includes spotty and lens-shaped uneven distribution of dolomite in the bed, abrupt variations in magnesium contents within small portions of a rock, a massive sugarlike rock habitus, and an assimilated fauna of a normal marine biocoenosis [4].

Many authors have linked the secondary dolomitization of limestones in the Pripyat trough with the sinking of intercrystalline brines of the salt-bearing beds into the subsalt and intersalt complexes. Our earlier studies [7] of the formation of highly concentrated chlorine-calcium brines of intersalt and subsalt deposits confirmed the transformation in these horizons of the brine of salt-bearing beds as they interact with carbonate rocks and scattered carbonates. Until now, however, the quantitative influence of this process on limestone dolomitization and the proportion of secondary porosity produced by this process remained unclear.

The principal factors determining the present composition of subsalt and intersalt brines and the alteration of carbonate rocks include the composition of the brine of the halogenous basin. For the hypothetical brines characterizing the Devonian halogenesis, one can take the composition of liquid inclusions in halite from rock salt of halogenous formations. By calculating the volumes of stratal water in subsalt and intersalt carbonate rocks, the total contents of calcium and magnesium in stratal brines of the lower hydrogeological story and the ratios of these cations in liquid inclusions from halite crystals, we attempted to determine the proportion of secondary porosity formed by catagenetic dolomitization of limestones.

The amount of magnesium from stratal water contributing to secondary dolomitization of subsalt and intersalt carbonate rocks was estimated with the formula

$$mMg = mMg_p - mMg_s$$

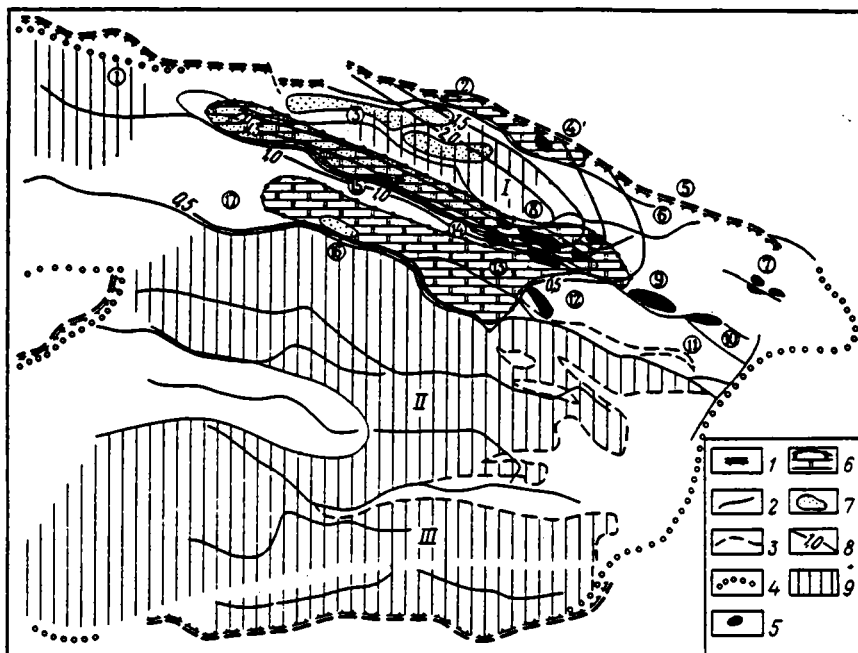


Fig. 1. Schematic lithohydrogeochemical map of the intersalt complex of Pripyat trough: (1-2) discontinuities (1 — marginal; 2 — regional); (3) the boundary of the zones with no intersalt sediments; (4) the wedging outline of salt-bearing strata; (5) oil deposits; (6) development areas of secondary dolomites in intersalt complex after [5]; (7) main occurrence areas of carnallite interlayers in the Upper Frasnian salt-bearing bed according to [1]; (8) isolines of potassium content in stratal waters of the intersalt complex, eq. %; (9) areas of occurrence of intersalt brines with a heightened magnesium content (5 eq. %) and lowered potassium content (0.3 eq. %); (I-III) structural-tectonic zones (I — northern; II — central; III — southern). Numbers identify the reconnaissance and exploration work localities: (1) Drozdovskaya, (2) Sudovitskaya, (3) Ozemlinskaya, (4) Berezinskaya, (5) Khatetskaya, (6) Ozershchinskaya, (7) Aleksandrovskaya, (8) Ostashkovichskaya, (9) Rechitskaya, (10), Krasnosel'skaya, (11) Barsukovskaya, (12) Zolotukhinskaya, (13) Southern Ostashkovicheskaya, (14) Southern Sosnovskaya, (15) Vishanskaya, (16) Oktyabr'skaya, (17) Chervonoslobodskaya.

where mMg is magnesium spent in secondary dolomitization, and mMg_p and mMg_s are the weight of magnesium in the previously subsided brine from halogenous basins and in Recent stratal waters of the intersalt and subsalt carbonate complex, respectively. Here

$$mMg_p = \frac{mCa + Mg}{1.66 \left(r \frac{Ca}{Mg} \right)_p + 1};$$

$$mMg_s = \frac{mCa + Mg}{1.66 \left(r \frac{Ca}{Mg} \right)_s + 1},$$

where $1.66 (r Ca/Mg) = m Ca/Mg$.

The increase of the primary porosity of the rocks of subsalt carbonate complex and intersalt complex associated with catagenetic dolomitization was estimated as

$$m = V_i/V,$$

where m is the proportion of secondary cavities, V_i is the volume of cavities formed by catagenetic dolomitization, and V is the volume of cavities in carbonate complexes. V_i is defined as

$$V_1 = \left(m \frac{\text{Mg}}{\text{CaMg}(\text{CO}_3)_2} / \gamma \right) n,$$

where $m\text{Mg}/[\text{Mg}/\text{CaMg}(\text{CO}_3)_2]$ is the weight of dolomite formed; γ , density of dolomite, set at $2.52 \cdot 10^3 \text{ kg/m}^3$; and n is limestone porosity after complete dolomitization equal to 12.5%, or 0.125.

Calculations showed that the decrease of magnesium content in stratal waters from values typical for brine inclusions in crystals of unaltered rock salt from Frasnian and Famennian salt-bearing strata to the current contents in stratal waters would raise the primary porosity by 0.5% in subsalt carbonate rocks and by 0.6% in the intersalt complex (Tables 1 and 2).

The actual porosity increase should be much greater, since the initial cavity volume was reduced by geostatic compaction of rocks during the time when the brine sank into carbonate strata. Studies of the interval-by-interval distributions of mean values of open porosity (a sample of 1354 determinations) of clayey limestone (dolomite) and marlstones of the intersalt complex in the Pripyat trough showed that the sinking of these rocks to the current depth of the subsalt and intersalt complexes could have reduced the porosity by a factor of 1.5-3.4 [2]. Stratal brines squeezed out by geostatic compaction of carbonate and carbonate-clay rocks of these complexes also contributed to dolomitization and increased the initial porosity.

Generalizing these data and calculations, one can state with certainty that catagenetic dolomitization of limestones altered by high-magnesium brines could have increased the initial porosity of intersalt and subsalt carbonate complexes by a few percentage points.

We will describe the main features of occurrence of secondary dolomites in the intersalt complex of the Pripyat trough. According to Makhnach et al. [5], the primary facies picture on most of the trough was not distorted by superimposed dolomitization processes. The sole exception is the northern structural tectonic zone, with areas composed of secondary dolomites and dolomitized limestones, which are often highly cavernous and fissured. These areas (see Fig. 1) are associated with the Rechitsa-Visha and Chervonoslobodka faults. The primary features of the rocks indicate their formation from organogenic-algal limestones, replaced along the course by dolomitized and clayey limestones that were little altered. In the northwestern part of the area (Starobinsk depression), where organogenic-algal limestones are less developed, the secondary dolomites are much less common. Within the occurrence areas of secondary dolomites, the degree of secondary dolomitization grows from southeast to northwest [6]. This is accompanied by a change in the contents of the individual components in stratal brines (see Fig. 1): a rise of potassium content with a lowered content of Mg and the ratio $r(\text{Mg}/\text{Ca})$. Such changes of the chemical composition of stratal waters are associated with the sinking into the intersalt complex of highly mineralized brine from the precipitation of potassium and potassium-magnesian salts and the substitution of brine magnesium for the calcium of the enclosing rocks in accordance with Heidinger and Marignac reactions. The specifics of this process were studied by us earlier [7].

The lithology and facies of the overlying salt-bearing bed support his interpretation of the factors accounting for the change of the composition of intersalt brines. In the eastern part of the trough, silvinite interlayers are absent in the salt-bearing bed. The total thickness and number of such interlayers increase in the northwestern direction [1]. A hydrogeochemical anomaly coincides in plan with the sites of occurrence of carnalite interlayers in the upper salt-bearing bed. The locations of the most intense catagenetic dolomitization of limestones are confined within the hydrogeochemical anomaly. Outside these areas, Mg content in stratal brines is usually higher. Combined with previous investigations, these facts suggest new criteria for predicting the sites of intense secondary dolomitization of limestones in territories with thick salt-bearing beds.

The lithologic criteria include (in addition to such conventional signs as heightened primary porosity and permeability, lower clay content of limestone, etc.) the development of potassium salts and carnallite interlayers in the overlying salt-bearing strata.

The hydrogeochemical criteria of secondary dolomitization in these regions include heightened potassium contents in the stratal waters of intersalt (subsalt) deposits associated with a lower magnesium content and lower values $r(\text{Mg}/\text{Ca})$ (see Fig. 1). Such hydrogeochemical anomalies indicate the presence of potassium-magnesian salts in the salt-bearing bed overlying the carbonate rocks and also intensiveness of metasomatic dolomitization in the carbonate rocks. Heightened potassium contents in stratal brines and lowered magnesium concentrations considered in isolation from each other cannot be regarded as indicative of the degree of secondary dolomitization of carbonate rocks.

The results of the study suggest the following conclusions.

1. The sinking of the parent brine of salt-bearing basins into subjacent carbonate sediments may produce a secondary dolomitization of limestones and increase the initial porosity of the rocks of these complexes on a regional scale by just a few percentage points.

2. New lithohydrogeochemical criteria for predicting the sites of intense catagenetic dolomitization of carbonate rocks in the regions with widespread halogeneous-carbonate formations are the following:

— the presence in the overlying salt-bearing bed of silvine-carnallitic rocks and minerals of a higher degree of condensation of seawater; and

— the presence of hydrogeochemical anomalies in carbonate complexes (horizons), manifested as heightened potassium content and lowered magnesium content.

3. A comprehensive investigation of lithologic and hydrogeochemical data makes it possible to describe in more detail the mechanism and features of catagenetic alteration of stratal brines and carbonate rocks and to appraise the effect of these processes on changing the capacity and infiltration properties of carbonate units.

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